ELSEVIER

Prog. Polym. Sci. 24 (1999) 425–480

PROGRESS IN
POLYMER SCIENCE

Driving forces in free radical addition–fragmentation processes

D. Colombani*

Faculté de Pharmacie, Université Victor Ségalen Bordeaux 2, 146, rue Léo Saignat, F-33076 Bordeaux Cedex, France

Received 3 April 1998; accepted 11 January 1999

Abstract

Advances and continuing challenges in achieving radical addition–fragmentation (AF) processes have resulted in an expanded understanding of the factors controlling both the addition and the fragmentation efficiency. Numerous works performed in recent years have offered the means for studying some structural constraints controlling the relative rates of intramolecular fragmentation over intermolecular propagation for the adduct radicals formed through addition on unsaturation. Comparison of sets of similar reactions may provide a reasonable guide to relative reactivities. The aim of this review is to discuss the factors which affect the rate and outcome of radical reactions most frequently encountered in radical AF processes. These reactions are generally believed to be mainly under kinetic rather than thermodynamic control, and a high degree of specificity can be exhibited by these radical processes when specific constraints are operative: steric hindrance (i.e. non-bonded interactions between radical and non-radical species), polar effects (relative electronegativities), stereoelectronic factors (i.e. requirement for overlap of frontier orbitals), and bond-strength (i.e. relative strengths of bonds formed or broken in the reaction). In this review, simple principles are provided for achieving greatly enhanced control of AF processes in most systems and for predicting the outcome of radical reactions. These rules may also help chemists in designing new AF agents and corresponding polymers.

Keywords: Addition–fragmentation process; Radical polymerization; Chain transfer; Functional polymers

Contents

* Corresponding author. Tel.: + 33-5-5757-1387; fax: + 33-5-5696-0975. This work was done in most part in the Institut Charles Sadron, UPR 22 CNRS, 6 rue Boussingault, F-67083 Strasbourg Cedex, France.

E-mail address: daniel.colombani@gnosie.u-bordeaux2.fr (D. Colombani)

0079-6700/99/$ - see front matter
PII: S0079-6700(99)00005-2

Nomenclature

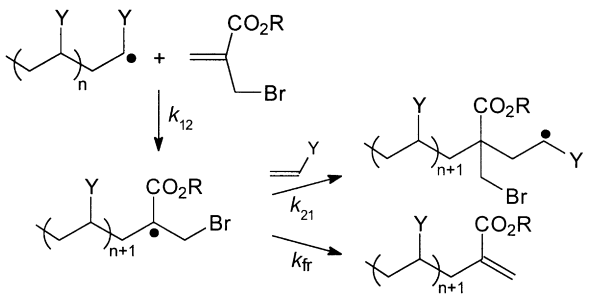
AF	addition–fragmentation
AFCT	addition–fragmentation chain transfer
AFCTA	addition–fragmentation chain transfer agent
AFM	addition–fragmentation monomer
AFP	addition–fragmentation polymerization
AIBN	2,2′-azobis(*iso*butyronitrile)
AN	acrylonitrile
BA	butyl acrylate
BDE	bond dissociation energy
Bu	butyl
Bz	benzyl
CTA	chain transfer agent
C_{tr}	chain transfer constant
DP_n	number-average degree of polymerization
EA	ethyl acrylate
E_a	activation energy
EC	ethyl cinnamate
EDG	electron-donating group
Et	ethyl
EWG	electron-withdrawing group
f	efficiency factor

HOMO	highest occupied molecular orbital
k	rate constant
LUMO	lowest unoccupied molecular orbital
MA	methyl acrylate
MAA	methacrylic acid
MAAm	methacrylamide
Me	methyl
MMA	methyl methacrylate
M_n	number-average molar mass
η	reaction coordinate
NMR	nuclear magnetic resonance
PD	*trans*-1,3-pentadiene
Ph	phenyl
PMMA	poly(methyl methacrylate)
Pr	propyl
PS	poly(styrene)
r_1	reactivity ratio of a monomer noted 1 versus another monomer (usually noted 2)
R_p	rate of polymerization
SEC	size-exclusion chromatography
S_Hi	intramolecular homolytic substitution
S_H2	bimolecular homolytic substitution
SOMO	singly occupied molecular orbital
St	styrene
T_c	ceiling temperature
Tol	tolyl
VA	vinyl acetate
σ^+	Hammett constant

1. Introduction

Addition–fragmentation (AF) reactions provide fascinating ability to do two things simultaneously in one reaction. The AF chain transfer regulates the chain length of addition polymers efficiently in such a way that functional groups are grafted at the ends of polymer chains. The AF polymerization involves control of polymer structure (i.e. backbone flexibility, functionality, solubility, and crosslinking index) through easy incorporation of alkyl-type fragments, bearing possibly some functionalities, which are not easy (or even possible) to introduce in usual polymer chains by any other method as the carbon skeleton of the monomeric unit is maintained intact in most vinylic polymerizations (i.e. ionic polymerization techniques). While the synthetic advantages of these approaches are clear, physical barriers exist between what may be designed and drawn on paper, and the practical reality.

The “chemical intuition” of experienced chemists often enables them to deduce the correct result arising from a reaction, and the products formed, with no apparent basis for conclusion. The aim of the present paper is to try and capture some of the rationale that guides chemists in reaching their conclusions and to present a few underlying principles that will help chemists (and non-chemists as well) in

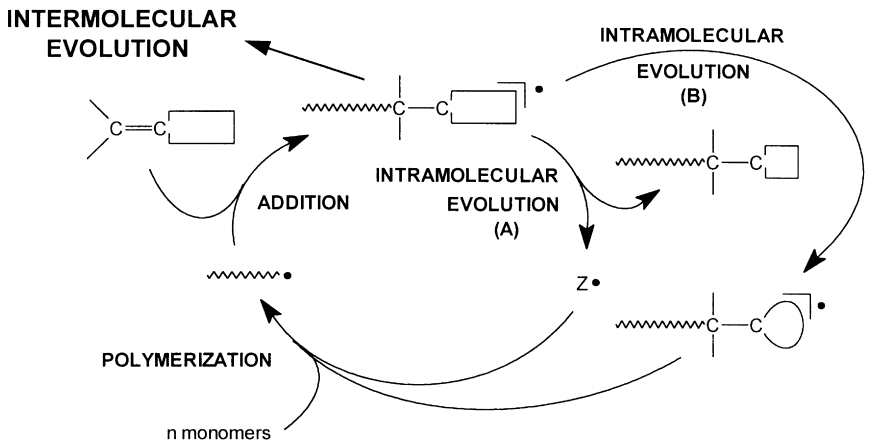


Scheme 1. Schematic representation of the competition between the fragmentation reaction (rate constant k_{fr}) and the copolymerization (rate constant k_{21}) of the adduct radical formed through addition on the double bond of an AFCTA (rate constant k_{12}).

perceiving the reactivity of AF agents in free radical polymerization. For this purpose, some of the subconscious filing system that has been necessarily developed over the years while acquiring data about chemistry is gathered here.

Thermochemical criteria have often been used in this regard, with assessment of radical processes being based on the relative stability of reactions, products, and intermediates. However, it can be seen that even for relatively simple systems, these criteria are often inadequate. The first step towards understanding the reactivity of an AF agent is to know the structural requirements needed for both efficient addition and fragmentation processes. The second step involves the correlation between the reaction conditions and the process needed. In most of the AF processes, the main problem originates from non-fragmented pendent groups that may greatly affect the physical properties of the polymer backbone. Further, when dangling unsaturations are present, they may even react with other growing chains, to afford crosslinked networks. This problem, inherent to the process itself, arises from competitive reaction paths involving the key radical intermediate (also referred to as radical adduct): (a) the desired intramolecular reaction (i.e. fragmentation), (b) the intermolecular cross-propagation with another monomer, or with the AF reagent itself (Scheme 1). The ratio of rate constants k_{fr}/k_{21} defines the fragmentation efficiency.

Unfortunately, AF reactions are much more complicated than indicated in Scheme 1, which does not do justice to the large amount of research carried out over the years in studying structural effects on AF agents. The present review focuses on factors that affect regio- and stereochemistry and the control selectivity in the addition of radicals on AF agents and in the evolution of radicals undergoing intramolecular rearrangement (i.e. fragmentation) leading to the incorporation of new structural isomer units into the polymer chain. Generalities regarding free radical polymerization are not discussed here; the reader is directed to the comprehensive compilations of Moad and Solomon, who have recently reviewed this important area [1]. Many papers dealing with AF reactions in both organic and polymer sciences are published each year, and it was not easy to select a few of these for inclusion into this article. The author's recent review [2] is a key reference, which summarizes hundreds of papers that appeared in this field up to 1996. Moreover, it is not my intention here to provide a new comprehensive overview, but rather to illustrate the main properties that we may expect in understanding and controlling the AF processes at the molecular level. The present survey attempts to give directions for using and discovering new synthetic-based principles for maximizing k_{fr}/k_{21}. The following issues are nearly always operative,



Scheme 2. Competition between inter- and intramolecular processes in the evolution of the adduct radical formed through the addition step.

even though their relative importance varies, and I hope that they will help chemists to gain an intuitive feel for the behavior of AF agents.

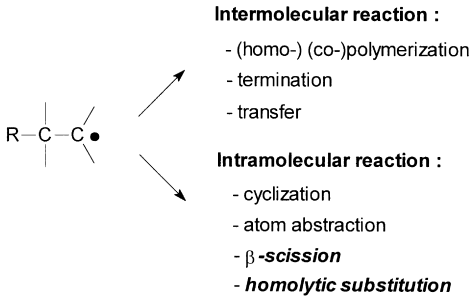
From a practical point of view, most of the chemistry is valuable for understanding why something happens (or not) after the fact, but the basic act of synthetic exploration, the discovery and extrapolation of new molecular compositions, ultimately leads to quantum leaps in understanding and application. This overview, then, endeavors to abstract results published in recent years in the synthetic investigation of AF reactions. We will see that some unexpected results often arise from accidental discoveries in synthesis and kinetic studies that have given new opportunities to explore molecular control of AF efficiency.

2. Driving forces: addition–fragmentation versus polymerization

The free radical addition of the propagating species to the alkenic double bond of an AF agent, and the subsequent fragmentation of the intermediate radical to afford a new radical (often called adduct radical), form the basis of free radical AF processes. The newly formed radical re-initiates the polymerization cycle [3]. During the process, a functional group may be formed on the backbone of the polymer (Scheme 2(A)) or at the end of the polymer chain (the new radical being attached to another molecular fragment, Scheme 2(B)). Either an AF (co)polymerization or an AF chain transfer are, respectively, involved in the two processes A and B cited before (Scheme 2).

AF processes compete with (co)polymerization when both the reactivity of the unsaturation and the fragmentation of the macroradical adduct on the AF agent are efficient. To fulfill this requirement, the presence of both an activated unsaturation and a low-dissociation-energy bond, located elsewhere on the molecule in a particular position, are required.

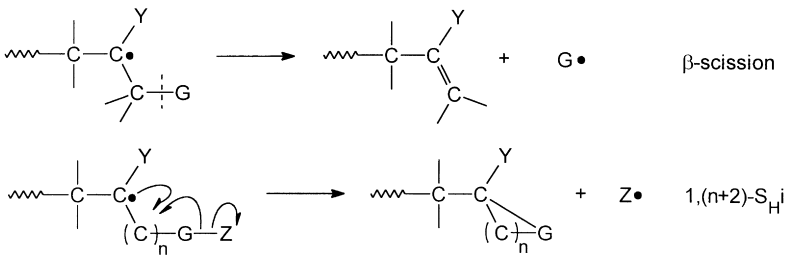
Several types of reactions are involved in the inter- or intramolecular evolution of the adduct radical provided by the addition step on an unsaturation (Scheme 3). Intermolecular reactions represent classical radical reactions, such as polymerizations (i.e. homo- and copolymerization, coupling and



Scheme 3. Potential inter- and intramolecular reactions of radicals in free radical polymerization.

disproportionation termination reactions, atom or group transfer through S_H2-type substitution). Radical rearrangements involved in free radical polymerization are generally intramolecular radical cyclization, atom and group transfer, β-fragmentation or 1,3 or 1,5-substitution. The two former processes have been extensively studied [4,5] and are not included in the present work. The β-scission and the β-peroxyalkyl rearrangement (i.e. intramolecular homolytic substitution noted as S_Hi) are cases which have been particularly studied in our laboratory (Scheme 4).

The kinetics of AF processes are particularly influenced by steric, polar and stereoelectronic factors, which direct the main mode of reaction of radicals, in determining the outcome of addition and homolytic intramolecular steps (i.e. overall reactivity and specificity) [6]. Whatever the fragmentation process may involve, it can compete effectively with propagation ($k_p \sim 10^2$–$10^3\ M^{-1}\ s^{-1}$), when the rate constant for the intramolecular homolytic evolution (e.g. β-scission or 1,*n*-S_Hi in most cases) is at least $\sim 10^5$–$10^6\ s^{-1}$. This means that more than 99% of fragmentation will lead to bulk polymerization. The best method to find potentially interesting reactions is to compare the regiochemistry of similar inter- and intra-molecular processes, and the rates of these two types of reactions as well. This comparison is often assessed in terms of the "effective concentration" of the neighboring group in the intramolecular reaction. This effective concentration is defined as the ratio of the rate constant of the intramolecular reaction to the rate constant of a suitable intermolecular model (k_{intra}/k_{inter}), whenever it exists [7]. For example, when a reactive species at low concentrations, such as a radical, reacts bimolecularly with 1 M substrate, the disappearance of the radical is pseudo first-order. If a related intramolecular reaction can be found, inherently first-order, which proceeds at the same rate, the effective concentration of the neighboring group in the intramolecular process will be 1 M. For example, rate constants of induced decomposition of allylic peroxides through homolytic intramolecular



Scheme 4. β-scission and intramolecular substitution in chain transfer reactions.

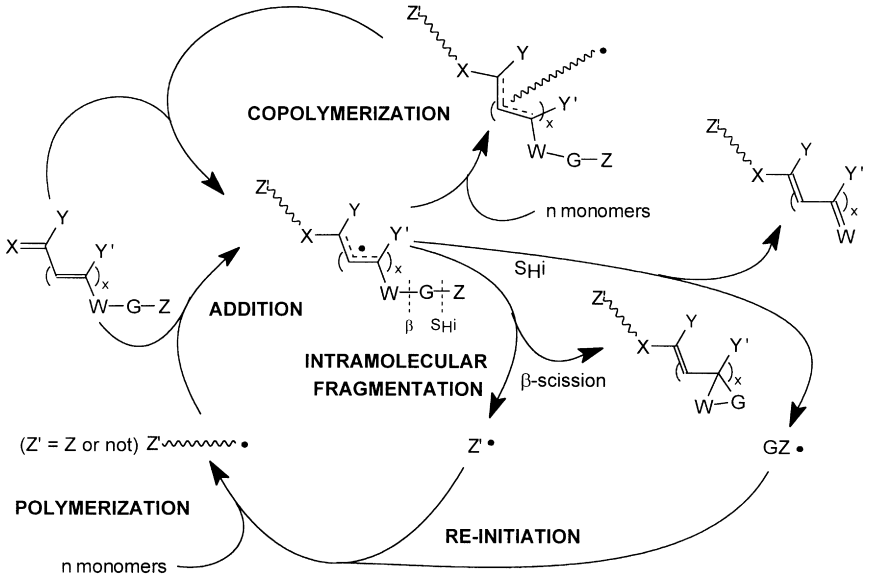
Table 1
Addition–fragmentation chain transfer agents (AFCTA) involved in free radical polymerization, through β-scission or homolytic substitution[a]

AFCTA	X	Y (Y′)	W	G	Z	Ref.
1	CH_2	CO_2Et	CHMe	O	OH	[9]
2a,b	CH_2	CO_2R[b]	CH_2	O	O*t*Bu	[10]
3a	CH_2	Ph	CH_2	O	O*t*Bu	[10]
3b	CH_2	Ph	CH_2	O	$OCMe_2Ph$	[10]
4	PhCH	CO_2Et	CH_2	O	O*t*Bu	[11]
5a	CH_2	CO_2Et	CHMe	O	OCH(OMe)OBu	[12]
5b	CH_2	CO_2Et	CHMe	O	$OCH(CH_2)_3O$	[13]
5c	CH_2	CO_2Et	CHMe	O	$OC(OMe)(CH_2)_5$	[14]
6a	CH_2	Ph	CHOMe	O	$OCMe_2Ph$	[15]
6b	CH_2	Ph	$CHOOCMe_2Ph$	O	$OCMe_2Ph$	[15]
7a	CH_2	CO_2Et	CHMe	O	$OSiMe_3$	[16]
7b	CH_2	CO_2Et	CHMe	O	$OSiMe_2CH=CH_2$	[16]
7c	CH_2	CO_2Et	CHMe	O	$OSiMe_2OOR$[c]	[16]
8a	CH_2	Me	C=O	O	O*t*Bu	[17]
8b	CH_2	Me	C=O	O	$OCMe_2Ph$	[17]
9a	CH_2	H (H)	CH_2	O	$OCMe_2Ph$	[18,19]
9b	CH_2	H (H)	CH_2	O	O*t*Bu	[19]
9c	CH_2	Me (H)	CH_2	O	O*t*Bu	[19]
9d	CH_2	Me (Me)	CH_2	O	O*t*Bu	[19]
9e	CH_2	Me (CO_2Me)	CH_2	O	$OCMe_2Ph$	[19]
10	MeCH	H (H)	CHOMe	O	$OCMe_2Ph$	[19]
11a	CH_2	CO_2Et	$(CH_2)_2CMeOMe$	O	$OCMe_2Ph$	[20]
11b	CH_2	C(=O)Me	$(CH_2)_2CMeOMe$	O	$OCMe_2Ph$	[20]
12	CH_2	H (H)	$(CH_2)_3$	O	$OCMe_2Ph$	[20]
13a	CH_2	Ph	O	CH_2	Ph	[21]
13b	CH_2	CN	O	CH_2	Ph	[22]
13c	CH_2	CO_2Me	O	CH_2	Ph	[22]
13d	CH_2	$CONH_2$	O	CH_2	Ph	[22]
14a	S		$(CH=CH)_2$	OC(=O)	$C_{15}H_{31}$	[23]
14b	S		$(CH=CH)_2$	OC(=O)	CH_2Ph	[24]
14c	S		$(CH=CH)_2$	OC(=O)	Ph	[24]
15a	S		S–CH=CH	OC(=O)	$C_{15}H_{31}$	[23]
15b	S		S–CH=CH	OC(=O)	CH_2Ph	[24]
16	S	Ph	O	CH_2	Ph	[23]
17a	CH_2	OEt	O	CH_2	Me	[25]
17b	CH_2	OMe	O	CH_2	Ph	[25]
17c	CH_2	OCH_2Ph-p-OH	O	CH_2	Ph-p-OH	[25]
18a,b	CH_2	CO_2R[b]	CH_2	Br	/	[26,27]
18c	CH_2	CO_2Et	CH_2	S	*t*Bu	[28,29]
18d	CH_2	CO_2Et	CH_2	S	$(CH_2)_2OH$	[28]
18e	CH_2	CO_2Et	CH_2	S	CH_2CO_2H	[28]
18f	CH_2	CO_2Et	CH_2	SO_2	Ph	[27,30]
18g	CH_2	CO_2Et	CH_2	SO_2	Tol	[30]
18h	CH_2	CO_2Et	CH_2	Sn	nBu_3	[27]
18i	CH_2	CO_2Et	CH_2	C	(SMe)CN	[29]
18j,k	CH_2	CO_2R[d]	CH_2	S	$(CH_2)_2OH$	[28]

Table 1 (*continued*)

AFCTA	X	Y (Y′)	W	G	Z	Ref.
19a	CH_2	CO_2H	CH_2 |	S	$(CH_2)_2OH$	[28]
19b	CH_2	CO_2H	CH_2 |	S	CH_2CO_2H	[28]
20a	CH_2	CN	CH_2 |	Br	/	[31]
20b	CH_2	CN	CH_2 |	S	*t*Bu	[32]
21a	CH_2	Ph	CH_2 |	Br	/	[27]
21b	CH_2	Ph	CH_2 |	S	tBu	[32]
21c	CH_2	Ph	CH_2 |	S	nBu	[27]
21d	CH_2	Ph	CH_2 |	S	$(CH_2)_2OH$	[28]
21e	CH_2	Ph	CH_2 |	S	CH_2CO_2H	[28]
21f	CH_2	Ph	CH_2 |	S	$(CH_2)_2CO_2H$	[28]
21g	CH_2	Ph	CH_2 |	S	$(CH_2)_2NH_2$	[28]
21h	CH_2	Ph	CH_2 |	S	$(CH_2)_2Si(OMe)_3$	[28]
21i	CH_2	Ph	CH_2 |	S(O)	*n*Bu	[27]
21j	CH_2	Cl	CH_2 |	S	*t*Bu	[33]
21k	CH_2	OC(=O)Me	CH_2 |	SO_2	Ph	[33]
22a	PhCH	CO_2Et	CH_2 |	Br	/	[11]
22b	PhCH	CO_2Et	CH_2 |	SO_2	Ph	[11]
22c	PhCH	CO_2Et	CH_2 |	S	*n*Bu	[11]
23	CH_2	H	CMe_2 |	C	$(NMe_2)COPh$	[29]
24	CH_2	H	CHPh |	C	$(NMe_2)COPh$	[29]
25	CH_2	Me	CMe_2 |	C	$(NMe_2)COPh$	[29]
26	CH_2	H	CH_2 |	C	(SEt)CN	[29]
27a	CH_2	CO_2Et	CH_2 |	OC(=O)	Ph	[29]
27b	CH_2	CO_2Et	CH_2 |	OC(=O) |	CH_2Ph	[29]
28	CH_2	CO_2Et	CH_2 |	C	$(NMe_2)CN$	[29]
29a,b	CH_2	CO_2Et	CH_2 |	C	$(SR)CN$[b]	[29]
30	CH_2	CO_2Me	CHPh |	C	$(NMe_2)COPh$	[29]
31	CH_2	CO_2Me	CHPh |	OC(=O) |	CH_2Ph	[29]
32a	CH_2	H (H)	CH_2 |	Br	/	[34]
32b	CH_2	Me (H)	CH_2 |	Br	/	[35]
32c	CH_2	H (Me)	CH_2 |	Br	/	[35]
32d	CH_2	Me (Me)	CH_2 |	Br	/	[35]
33a	CH_2	H (H)	CH_2 |	S	*t*Bu	[29,36]
33b	CH_2	Me (H)	CH_2 |	S	*t*Bu	[35]
33c	CH_2	H (Me)	CH_2 |	S	*t*Bu	[35]
33d	CH_2	Me (Me)	CH_2 |	S	*t*Bu	[35]
34	CH_2	H (H)	CH_2 |	SO_2	Ph	[34]
35	CH_2	H (H)	CH_2 |	C	(SMe)CN	[29]
36a	CH_2	Me (CO_2Me)	CH_2 |	Br	/	[34]
36b	CH_2	Me (CO_2Me)	CH_2 |	S	*t*Bu	[29]

[a] Fragmentable bonds are indicated by a dotted line between atoms or groups involved.
[b] R = Me (**a**), Et (**b**).
[c] R = $CHMeC(=CH_2)CO_2Et$.
[d] R = $(CH_2)_2OH$ (**j**), 2-phtalylCH_2 (**k**).



Scheme 5. Mechanism of the AFCT reaction in free radical polymerization, through β-scission or homolytic substitution.

substitution (i.e. 1,3-S_Hi) by PS· and PMMA· macroradicals are several orders of magnitude (ca. four orders) higher than the rate constants of intermolecular S_H2 for ordinary dialkyl peroxides. Indeed, chain transfer constants of di-*tert*-butylperoxide and di-*iso*-propylperoxide in styrene polymerization at 60°C are as low as $2–13 \times 10^{-4}$ and 3×10^{-4}, respectively [8].

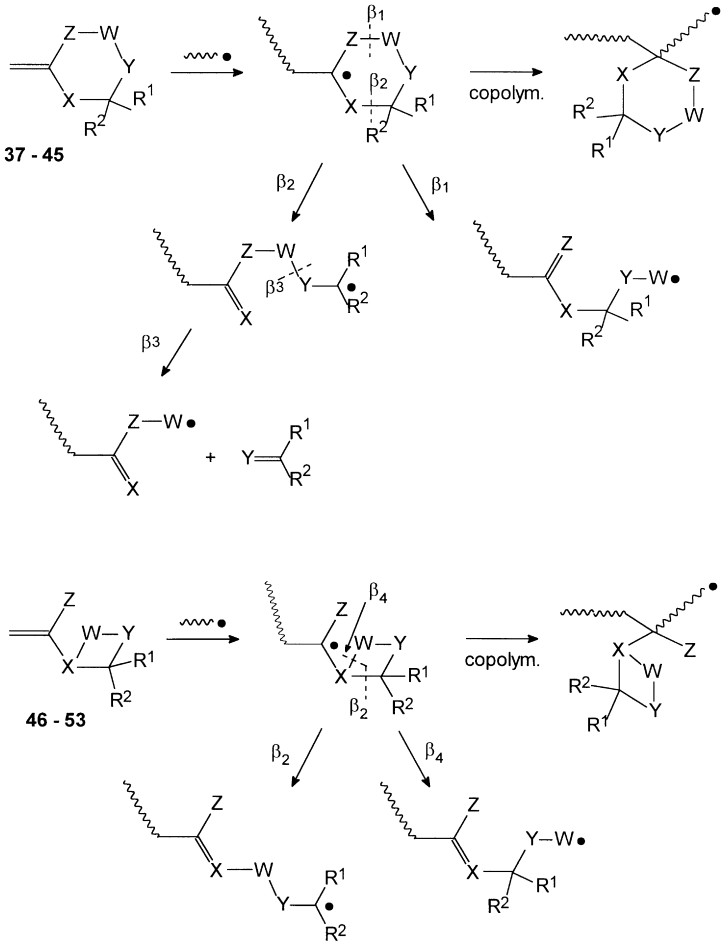
There are some reactions which have no intermolecular counterpart. For β-scission, a comparison between inter- and intramolecular reaction cannot be investigated. In this case, the kinetic advantage of intramolecularity makes these reactions observable.

2.1. Structural requirements for fragmentation

Regardless of the effect influencing the outcome of the AF process, the driving force for fragmentation has to be high enough to compete with propagation. The various trends, that are generally investigated to enhance the fragmentation step, are briefly listed later. Either the steric hindrance can be increased in the intermediate free adduct radical to inhibit almost totally the possibility of copolymerization (Section 2.2.2) or a small strain can be introduced in the transient radical in order to force its fragmentation (Section 2.1.2). The intramolecular process may also be favored by the formation of a more stable radical (Section 2.1.4) than the adduct radical formed through addition or more simply by choosing higher polymerization temperatures (Section 3.1) or dilutions (Section 3.2).

2.1.1. Nature and size of the labile fragment

Scheme 5 and Table 1 summarize most of the usual leaving groups used in AF chain transfer reactions. Bromine atoms, thioderivative radicals (i.e. SR, SO_2Ar,…), alkoxyl radicals (formed through peroxydic or activated ether homolysis), and some carbon radicals substituted by both electron-donating and -withdrawing groups (Section 2.1.4, dealing in part with captodative leaving fragments) afford



Scheme 6. Mechanism of the AF polymerization, through β-scission as intramolecular evolution.

efficient fragmentation reactions. Breaking bonds (through β-scission or 1,3-S_Hi) have been symbolized by a dotted line between either W and G groups (β-scission) or G and Z groups (1,3-S_Hi). Another dotted line has been used to indicate a possible further elimination of a molecule of CO_2. We will see in Section 2.1.6 that the elimination of a stable molecule is an important driving force for the fragmentation reaction.

In the case of AF monomers, two main types of reagents have been identified, according to their reaction mechanism: those involving the rupture of a X–W linkage (i.e. vinyl cycloalkanes and vinyloxiranes) and those involving the fragmentation of a Z–W bond (i.e. cyclic ketene acetals, cyclic enol ethers, cyclic ortho-carbonates and ortho-esters, β-oxo-α-methylenelactone, γ-thio-α-methylene lactone) (Scheme 6 and Table 2). In both cases, the possibility of fragmentation between X and CR^1R^2 has been considered. The sites of potential fragmentation are mentioned in Scheme 6 and is also symbolized in Table 2 by a dotted line between the atoms or groups involved. Similar to the former case, a second dotted line has been drawn when a further radical fragmentation is operative. It is mentioned only when it is of particular interest (e.g. scission β_3, Scheme 6).

Table 2
Addition–fragmentation monomers (AFM) involved in the free radical polymerization, through β-scission as the intramolecular rearrangement[a]

AFM	Z	W	X	CR^1R^2	Y	Ref.
37a	O	CH_2	O |	CH_2	/	[37]
37b	O |	CH_2	O	CH_2	CH_2	[37]
37c	O |	CHMe	O	CHMe	CH_2	[38]
37d	O |	CH_2	O	CH_2	$(CH_2)_2$	[39]
37e	O	CHMe	O |	CHMe	$(CH_2)_2$	[41]
37f	O	CH_2	O |	CH_2	$(CH_2)_3$	[40]
37g	O	CH_2	O |	CHPh	/	[41,42]
37h	O |	CH_2	O	CHPh	CH_2	[40]
37i	O |	CH_2	NMe	CH_2	/	[43]
37j	O	CH_2	S |	CH_2	/	[44]
37k	O |	CH_2	O	$=CH_2$	/	[45]
37l	O |	CH_2	O	CH_2	$=CH_2$	[45]
37m	O |	/	O	CHMe	CHMe	[38]
37n	O |	/	O	CHPh	CHPh	[38]
38	O |	CH_2	O	CH_2	$CH_2OC(=CH_2)OCH_2$	[46,47]
39	O |	CH_2	O	CH_2	$-\underline{CHOCMe_2OC}H-$	[47]
40a	C=O	O	O |	CHPh	/	[48]
40b	C=O	O	O |	CMe_2	/	[48]
40c	C=O	O	O |	CH_2	CH_2	[48]
40d	C=O	O	O |	CHPh	CHPh	[48]
40e	C=O	O	O |	CHMe	CHMe	[48]
41a	CH_2 |	S	CO_2	CH_2	CH_2	[49,50]
41b	CH_2 |	S	CO_2	CH_2	$(CH_2)_5$	[49]
41c	CH_2 |	S	CO_2	CH_2	$(CH_2)_4OCOCH_2$	[49]
41d	CH_2 |	S	CO_2	CH_2	CHMe	[49]
41e	CH_2 |	S	CO_2	CH_2	$(CH_2)_2OCH_2$	[49]
41f	CH_2 |	SO_2	CO_2	CH_2	$(CH_2)_4OCOCH_2$	[49]
41g	CHMe|	S	CO_2	CH_2	CH_2	[50]
41h	CH_2 |	S	CO_2	CH_2	$CH_2NMe(CH_2)_2$	[51]
41i	CH_2 |	S	CH_2S	CH_2	CH_2	[52,53]
41j	CH_2 |	S	CH_2S	CH_2	$(CH_2)_2$	[52,53]
41k	CH_2 |	S	CH_2S	$CHCH_2OH$	CH_2	[33]
41l	CH_2 |	S	CH_2S	$CHCH_2O_2CCH_3$	CH_2	[33]
41m	CH_2 |	S	CH_2S	$CHCH_2O_2CC(Me)=CH_2$	CH_2	[33]
42a	CH_2 |	O	CH_2O	$C[OCH_2C(=CH_2)CH_2O]$	/	[54,55]
42f	CH_2 |	O	CH_2O	$C[OCH_2CMe_2CH_2O]$	/	[57]
42g	CH_2 |	O	CH_2O	$C[OCH_2\text{-}1,2\text{-}C_6H_4\text{-}CH_2O]$	/	[57]
42h	$(CH_2)_2$|	O	CH_2O	$C[OCH_2\text{-}1,2\text{-}C_6H_4\text{-}CH_2O]$	/	[57]
42b	CH_2 |	O	O	$C[OCH_2\text{-}1,2\text{-}C_6H_4\text{-}CH_2O]$	/	[56]
42c	CH_2 |	O	O	$C[OCH_2\text{-}1,2\text{-}C_6H_4\text{-}CH_2O]$	/	[57]
42d	$(CH_2)_2$|	O	O	$C[OCH_2\text{-}1,2\text{-}C_6H_4\text{-}CH_2O]$	/	[57]
42e	$(CH_2)_3$|	O	O	$C[OCH_2\text{-}1,2\text{-}C_6H_4\text{-}CH_2O]$	/	[57]
43a	CH_2 |	O	O	$O(CH_2)_3$	/	[58]
43b	CH_2 |	O	O	$C[O(CH_2)_4]$	/	[58]
43c	CH_2 |	O	O	$C[O(CH_2)_5]$	/	[58]
43d	CH_2 |	O	O	$C[O\text{-}1,4\text{-}C_6H_{10}]$	/	[58]

Table 2 (*continued*)

AFM	Z	W	X	CR^1R^2	Y	Ref.
43e	CH_2	O	O	$C[OCH_2\text{-}1,2\text{-}C_6H_4]$	/	[59]
43f	CH_2	O	O	C(Ph)OMe	/	[60]
44a	CH_2	CH_2	O	CH_2	/	[61,62]
44b	CH_2	CH_2	O	CH_2	CH_2	[38]
44c	CH_2	CH_2	O	CHPh	/	[38]
44d	CHMe	CH_2	O	CH_2	/	[38]
44e	CH_2	/	O	CH_2	/	[38]
45a	CH_2	O	O	CH_2	/	[38]
45b	CH_2	O	O	CPh_2	/	[38]
45c	CH_2	O	O	CHPh	/	[63]
45d	CH_2	O	O	$CH(o\text{-}ClC_6H_4)$	/	[64]
45e	CH_2	O	O	C(Ph)OMe	/	[65]
45f	CH_2	O	O	$C(C_6H_4\text{-}p\text{-}R)_2$[b]	/	[66]
45g	CH_2	O	O	$C[\text{-}1,2\text{-}C_6H_4\text{-}1,2\text{-}C_6H_4\text{-}]$	/	[67]
45h	CH_2	O	O	CPhMe	/	[68]
46a	H	CH_2	CH	CH_2	/	[69]
46b	H	CH_2	CH	CHCl	/	[70]
46c	H	CH_2	CH	CCl_2	/	[71,72]
46d	H	CH_2	CH	$CHCO_2Et$	/	[73]
46e	H	CH_2	CH	$C(CO_2Et)_2$	/	[74,75]
46f	Me	CH_2	CH	$C(CO_2Et)_2$	/	[76,77]
46g	H	CH_2	CH	$C(CN)CO_2Et$	/	[76]
46h	H	CH_2	CH	$C(CO_2R)_2$[c]	/	[78,79]
46i	H	CH_2	CH	CHPh	/	[80]
46j	H	CH_2	CH	$C(Ph)CO_2Et$	/	[73]
46k	H	CH_2	CH	$C[CH_2OCO_2CH_2]$	/	[81]
46l	cC_3H_5	CH_2	CH	CH_2	/	[82]
46m	H	CH_2	CH	CF_2	/	[83,84]
47a	Ph	CH_2	CH	CH_2	/	[85]
47b	$p\text{-}ClC_6H_4$	CH_2	CH	CH_2	/	[85]
47c	p-MeOPh	CH_2	CH	CH_2	/	[85]
48a	$OSiMe_3$	CH_2	CH	CH_2	/	[86]
48b	$OSiMe_3$	CH_2	CH	CHPh	/	[86]
49a	H	CH_2	Me_3SiOCH	$CHCO_2Et$	/	[86]
49b	H	CH_2	Me_3SiCH_2CH	$CHCO_2Et$	/	[87]
49c	Me	CH_2	MeCH	$C(CO_2Et)_2$	/	[77]
50a	H	CH_2	CH	$C[O(CH_2)_2O]$	/	[88]
50b	H	CH_2	CH	$C[O(CH_2)_4O]$	/	[88]
50c	H	CH_2	CH	$C[O\text{-}CHPh\text{-}CH_2\text{-}O]$	/	[88]
50d	H	CH_2	CH	$C[O\text{-}1,2\text{-}C_6H_4\text{-}O]$	/	[88]
50e	H	CH_2	CH	$CHCO_2Me$	$CHCO_2Me$	[89]
51a	H	O	CH	CH_2	/	[90]
51b	H	O	CH	CHPh	/	[91]
51c	Me	O	CH	CHPh	/	[92]
51d	H	O	CH	$CHC_6H_4\text{-}p\text{-}R$[b]	/	[91]
51e	H	O	CH	CH-furyl	/	[93]
52a	H	SO_2	CH	CH_2	$(CH_2)_2$	[94]
52b	H	SO_2	CH	CH_2	$(CH_2)_3$	[94]

Table 2 (*continued*)

AFM	Z	W	X	CR^1R^2	Y	Ref.
52c	H	SO_2 |	CH	CH_2	$(CH_2)_4$	[94]
52d	H	SO_2 |	CH	CH_2	$(CH_2)_2CHPh$	[95]
52e	H	S |	CH	CH_2 |	/	[96,97]
53	H	O |	CH	CHPh |	C=O	[95]

[a] Fragmentable bonds are indicated by a dotted line between atoms or groups involved.
[b] R = Me, Ar, MeO, Cl, CN.
[c] R = Ph, Adamantyl.

Alkyl and fluoromethyl or alkoxymethyl fragments located in the α position with respect to the unsaturation do not induce fragmentation under the usual reaction conditions of radical polymerization. Chlorine atoms and phenoxyl groups located on a methylene fragment exhibit borderline behavior, particularly restricted to reaction conditions. This latter point is discussed specifically in more detail in Section 3.

Concerning the relative reactivity of α-(halomethyl)acrylic reagents, Yamada and Otsu [98] have attempted to correlate the size of the halogen atom with the reactivity of these compounds through the competition between fragmentation (rate constant k_{fr}) and (co)polymerization (rate constant k_{21}). They proposed that the occurrence of AF may be correlated to the steric hindrance of the halogen atom. Taft's steric substituent constant (E_s) and Hammett's polar substituent constants [99] (σ^+) were shown to vary slightly with the nature of the halomethyl groups, even though the CH_2Br group was expected to be larger than the CH_2Cl group, and the electron-withdrawing effect of the chlorine atom higher than that of the bromine (Table 3). On the contrary, the Van der Waals radii [100] ($r_{CH2} + r_X$) of the bromomethyl group appears effectively larger than the chloromethyl and the fluoromethyl group, which is in agreement with common sense. However, as reported by the authors, it is not yet absolutely clear if the steric effect may be considered as the main factor for interpreting the observed tendencies in α-(halomethyl) acrylates.

The reactivity of α-halomethylacrylates and, more generally, the difficulty of 1,2-polymerization of most of the 1,1-disubstituted vinylic-type AF agents can be illustrated in part by comparison with their parent 1,1-disubstituted monomers, upon replacing the heteroatom O, S, or N by a CH_2 and checking the polymerizability of the resulting olefins. It appears that these latter monomers are also reluctant to homopolymerize. For example, methyl α-alkylsubstituted acrylates $H_2C{=}C(R)CO_2Me$ with

Table 3
Polar and steric substituent constants and the size of the halomethyl group in α-(halomethyl)acrylic reagents (taken from Ref. [101])

Halomethyl group	σ^+[99]	$-E_S$ [99]	($r_{CH_2} + r_X$) (Å) [100]
CH_2Br	0.14	1.51	2.98
CH_2Cl	0.12	1.48	2.88
CH_2F	0.11	1.48	2.60
CH_3	− 0.17	1.24	2.23
CH_2CH_3	− 0.15	1.32	3.43

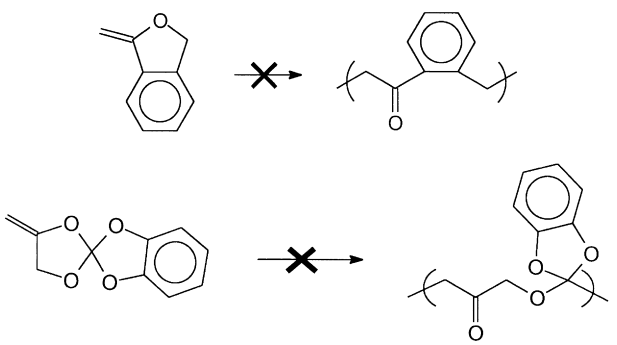
R=$CH(CH_3)_2$, $CH(CH_3)CH_2CH_3$ or $CH_2CH(CH_3)_2$ do not homopolymerize [102]. A conventional explanation for the difficult radical polymerization of 1,1-disubstituted olefins is the known lowering effect of bulky substituents on the ceiling temperature (T_c). One classical example of this effect is α-methylstyrene ($T_c < 30°C$), and reported T_c values for MMA and methyl 2-ethylacrylate are ca. 241°C and 73°C ([monomer] = 8.35 M), respectively [103]. Such a thermodynamic limitation is one of the factors which may favor the occurrence of the AF reaction, in comparison with homopropagation. It can also account for the molecular design of most AF reagents, which always favors the steric hindrance of the intermediary adduct radical, formed through the addition step. On the contrary, it may also afford an answer to the good reactivity of some AF monomers when they are homopolymerized, and their low fragmentation efficiencies when copolymerized with common 1,2-vinylic monomers. In the latter case, the ratio k_{fr}/k_{21} becomes lower because of an increase in the copolymerization rate constant k_{21}.

2.1.2. Relief of strain

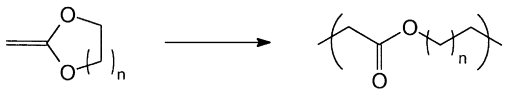
AF processes, as many radical reactions, preferentially follow the most exothermic pathway and the relief of strain is often claimed to be one of the main factors affecting the competition between fragmentation and propagation reactions. Though thermochemical criterias are often used to rationalize or predict the outcome of radical reactions, other effects may influence the reaction. The fragmentation efficiency may be particularly influenced by stereoelectronic factors and substitution patterns in the transition state of the rearrangement. These effects, discussed in the following section, often dominate over thermodynamic factors.

2.1.2.1. Stereoelectronic factors In strained structures, the molecular flexibility needed for adopting an appropriate conformation for the intramolecular reaction leading to fragmented structures cannot be obtained in the presence of some rigid connecting groups. For example, a clear demonstration that C–O bond homolysis adjacent to a radical center is stereoelectronically controlled is provided by the 1,2-polymerization of olefins mentioned in Scheme 7. In these cases, thermochemical effects are totally dominant, even though in the first example, fragmentation of the ring would provide both a carbonyl function and a primary radical conjugated with the phenyl ring. Such a limitation arises from the fact that it is harder for the intermediate radical issued from addition to adopt the correct conformation for fragmentation than for intermolecular propagation (Scheme 7) [61,104].

The aforementioned examples are typical examples of the importance of stereoelectronic effects in the



Scheme 7. Examples of strained olefins exhibiting no ring-opening when radically polymerized.



37a,d

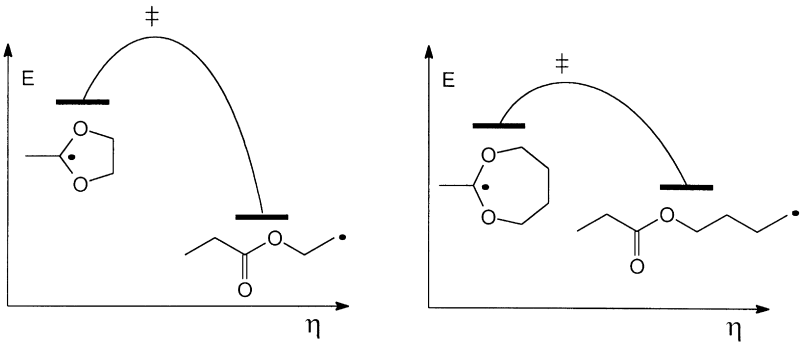
Scheme 8. AF polymerization of exomethylene cyclic ketene acetals **37a,d**.

outcome of radical reactions. They mainly result from conformational constraints on the geometry of the transition state resulting from the energy requirement for maximum electron delocalization. Indeed, the lowest energy is always exhibited in the preferred transition state of a reaction. In this case, the requirement of maximum delocalization of the electrons is attained in the absence of steric constraints by a particular orientation of molecular orbitals, i.e. a specific geometry of the intermediate species in the transition state. The result of reactions which are attributed to this restricted geometry of the transition state are termed as stereoelectronic effects. Most of the homolytic reactions, occurring on strained molecules through the thermodynamically less favorable reaction pathway, are stereoelectronically controlled. It is the case for the C–C bond homolysis, adjacent to a radical center, commonly referred to as β-scission. The transition state for β-scission is specifically formed by an initial coplanar interaction of the semi-occupied p orbital of the radical with the σ* antibonding orbital of the bond undergoing scission (*note:* the spatial orientation of a bond is equivalent to that of its σ* antibonding orbital). In such a case, the transition state may be considered to involve initial coplanar interactions of the semi-occupied p orbital with the bond undergoing scission. These rearrangements provide evidence that, in the fragmentation of a C–C bond adjacent to a radical center, the bond which can meet the maximum degree of coplanarity with the semi-occupied p orbital of the radical is stereoelectronically favored to break the transition state

Consider, as another example, the AF polymerization of cyclic ketene acetals **37**. Stereoelectronic effects on the fragmentation of C–O bond adjacent to a semi-occupied p orbital have also been invoked to explain the preferred β-scission of the transient radical obtained through addition of **37** to form the ester function. This kind of compound fragments is predominant in the seven-membered ring form (**37d**, $n = 3$), than in the cyclopentyl one (**37a**, $n = 1$) (Scheme 8).

In the case of five-membered cyclic ketene acetals, there is a special effect which has to be mentioned: a ring-strain is imposed by geometric requirements for orbital overlap in the transition state. Clearly, it appears that the importance of favorable orbital overlap at the transition state of the AF polymerization of cyclic monomers, which in this example increase the outcome of the reaction of the thermodynamically less stable strained ring, have to be considered in conjunction with thermochemical criteria when predicting and/or rationalizing the outcome of free radical reactions. Thus, the energetically preferred coplanar interaction of the semi-occupied p orbital of the planar radical center and the σ* antibonding orbital of the C–O bond is more likely to occur in the cycloheptyl-type AFM **37d** than in the cyclopentyl-type AFM **37a**, in which the strain constraints are quite obvious.

The behavior of the reaction could not be predicted from an energetic point of view. This may be considered as an example of “crossing” reaction profiles (reported for two different molecules in this case), as the five-membered cycloalkane ring is generally more strained than the seven-membered ring. This is conveniently illustrated in Scheme 9. As in all other exothermic reactions, the transition state is closer to the reactants than to the products, along both the coordinate axes.

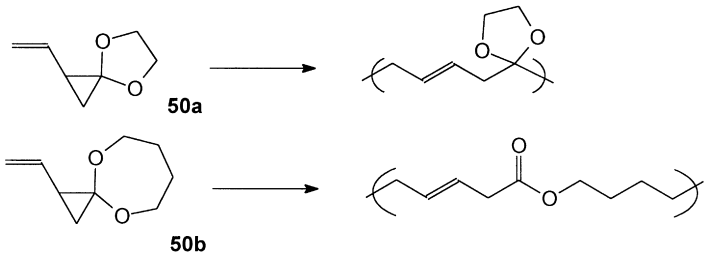


Scheme 9. Energetic diagram of "crossing" reaction for **37a,d**.

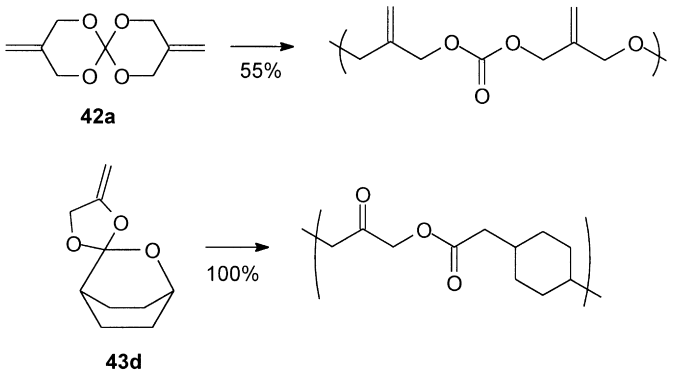
The need for stereoelectronic conformations to get efficient β-scission is also an explanation which is often invoked for the greater easiness of fragmentation in larger ring systems. For more detailed information on stereoelectronic effects in free radical reactions, the reader is referred to the review of Beckwith [105].

Another important point is that stereoelectronic effects are independent of the mode of production of the radical which is involved in the process. It either results from a simple addition reaction or from a preliminary radical cascade. For example, vinylcyclopropanone cyclic acetals **50a–d** may be regarded as hybrid monomers consisting of 2-vinylcyclopropyl fragments grafted on the carbon located between the two oxygen atoms of the cyclic ketene acetal moieties (after the addition step on the unsaturation, a subsequent cyclopropane scission affords a radical similar to the preceding case) [85]. The structures of the polymers resulting from radical polymerization of **50a–d**, dramatically change according to the ring size and the substitution pattern of the monomers, but obey the general principle of fragmentation described earlier for simple cyclic ketene acetals **37**. For instance, radical polymerization of **50a** affords mainly single ring-opened units whereas poly(**50b**) mainly consists of double ring-opened units (Scheme 10). Comparated to these latter examples, six-membered rings in ketene acetals and related AF monomers fragment radically only if additional driving force is present to promote the scission step.

An additional driving force for the double fragmentation of cyclic spiro-orthocarbonates and spiro-orthoesters, thermally polymerized in bulk to high conversion, comes mainly from the strain relief at the central spiro atom. A substantial contribution from the formation of a stable carbonyl group should also be taken into account (Section 2.1.4) [107]. The range of the degree of fragmentation of rings (0–90%) may also be explained by other factors (e.g. polymerization temperature, steric hindrance of the monomer, stability of formed radicals, and differences in activation energies between competitive reactions). For example, a higher temperature yields polymers with a higher degree of fragmentation (Section 3.1). In all cases, the obtained macromolecular structures exhibit two monomeric repeat units derived from both addition-(double scission) polymerization and vinylic polymerization. For example, 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane **42a** polymerizes at 180°C to produce 90% yield of the corresponding polymer. Moreover, the degree of addition-double fragmentation is only 55% (Scheme 11). Similarly, polymers of some exomethylene spiro-orthoesters **43** (e.g. 2-methylene-1,4,6-trioxaspiro [4,4]-nonane **43a** or its seven-membered cycle parent **43c**) [108] yield polymers with complex structures, indicating that stereoelectronic effects disfavor exclusive fragmentation under the reaction



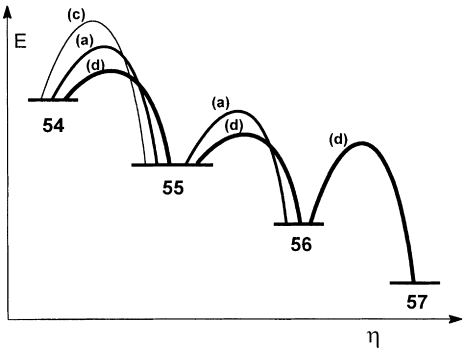
Scheme 10. AF polymerization of vinylcyclopropanone cyclic acetals **50a,b** in bulk at 60°C [85,106].



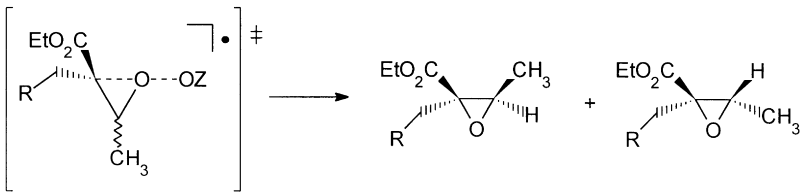
Scheme 11. Addition-(double fragmentation) polymerization of **42a** and **43d**.

conditions used [109]. Complete double fragmentation occurred only with a more strained unsaturated spiro-orthoester **43d** (Scheme 11).

A proposed profile of the energetic diagram of the cascade fragmentation resulting from the homopolymerization of cyclic spiro-orthoesters **43a,c,d** is given in Scheme 12, in which only the relative order of the energetic levels have to be considered. The importance of the transition state activation energy and the ground-state energy level of radicals **54–57** have been roughly estimated in each case from the percentage of fragmentation units obtained and from the strain of the molecule. Moreover, the



Scheme 12. Energetic diagram of the cascade fragmentation of the AF polymerization of cyclic spiro-orthoesters **43a,c,d**.



Scheme 13. Transition state affording stereoselectivity through intramolecular homolytic substitution in the induced decomposition of allylic peroxides **5a–c**.

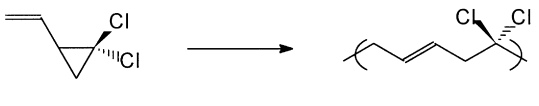
intermediate adduct radicals **54** seems largely influenced by the strain of the monomer to promote the occurrence of the fragmentation [108]. The five-membered ring of the bicyclic spiro-orthoesters predominantly fragments when the adjacent cycle is cyclopentyl (**54**, $n = 3$), rather than when it is the isomeric seven-membered form (**54**, $n = 5$). In the case of the polymerization of **43d**, the additional driving force due to the strained structure can overlap the stereoelectronic constraints to fragment the two rings efficiently.

Beckwith et al. demonstrated the dominant role of stereoelectronic factors as the requirement for an alignment of the orbital bearing the attacking unpaired electron and both oxygens of the O–O bond in the transition state [110,111] (Scheme 13). Such a requirement involves an allylic strain on the transient radical which is highly dependent on its conformation when substituents are present between the addition and the fragmentation site. This strain effect affords a degree of stereoselectivity in the intramolecular homolytic substitution [112]. In Scheme 13, the transition states leading to both *Z* and *E* isomers in the homolytic induced decomposition of ethyl α-peroxymethylacrylates **5a–c** are shown.

This co-linear arrangement is also operative in the intramolecular 1,5-H atom transfer for which a six-membered transition state has been proposed. The chair conformation implies the required arrangement of atoms in the transition state for 1,5-atom transfer. In smaller or larger rings, such a transition state cannot be readily achieved. Indeed, significant strain is inherent to the small rings, whereas severe non-bonding interactions or less favorable entropy of activation occur for large rings [113,114].

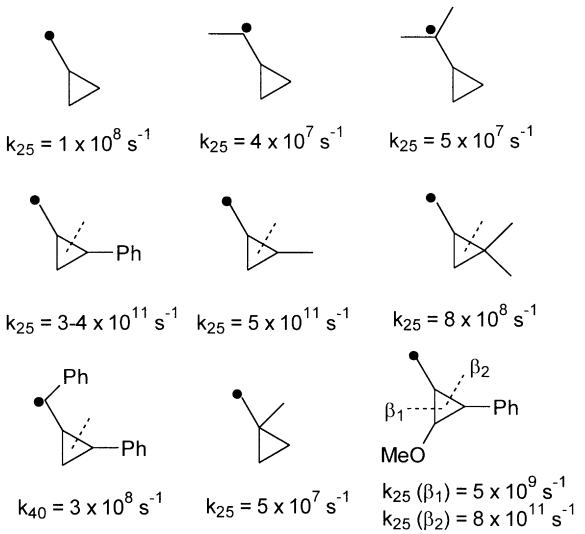
Several research groups [115] have also investigated the elementary ring-opening of three-membered ring structures, e.g. cyclopropylmethyl radical and related species, to polymerize new monomers **46–50** through the formation of isomeric homoallylic radical (Scheme 14).

The strain relief of the cycle and the stabilization of the formed radical provide the main driving force for the fragmentation [116]. Indeed, three-membered rings (e.g. vinyl cycloalkanes **46–50**) exhibit high ring-strain, affording facile exothermic fragmentation ($\Delta H^{o} = -20\ \mathrm{kJ\ mol^{-1}}$) of the adduct radical formed by addition to the unsaturation. Rates of fragmentation of cyclopropylmethyl radical derivatives are very fast, ca. 10^{5}–$10^{8}\ \mathrm{s^{-1}}$, depending on the substitution pattern (Scheme 15) and the polymerization of cyclopropylvinyl derivatives give generally 100% fragmentation of the ring. The presence of an



46c

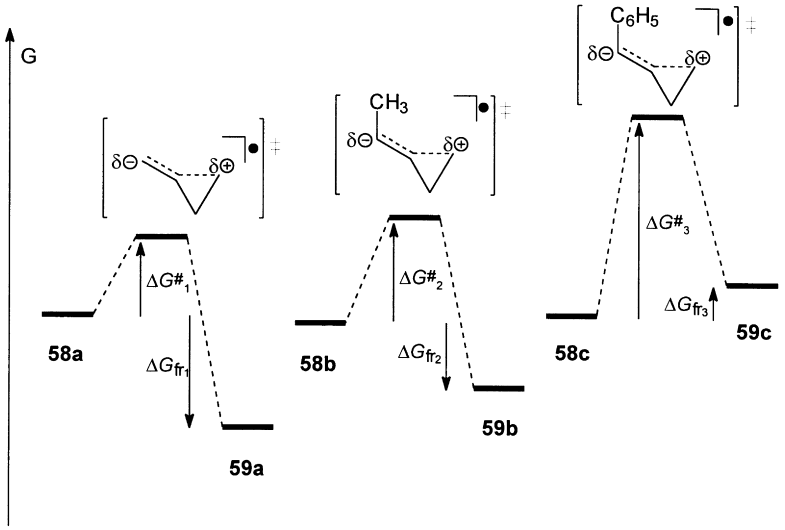
Scheme 14. Selective cleavage of a C–C bond in the AF polymerization of 1-vinyl-2,2′-dichlorocyclopropane **46c**.



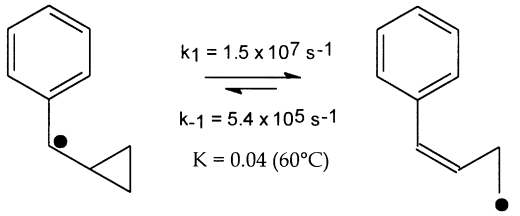
Scheme 15. Rates of fragmentation of cyclopropylmethyl radical derivatives [116].

α-substituent influences the fragmentation efficiency of cyclopropylmethyl radical derivatives **58b**,**c** through steric hindrance with the ring.

The reversibility of the fragmentation is often considered to explain the low polymerization rates observed, especially when an α-aryl substituent activates the unsaturation (*note:* the reverse reaction is exocyclization). In the latter case, the rates of fragmentation of monomers **47a–c** are reduced by a factor of ca. 10^2–10^3 compared to the corresponding non-substituted vinylcyclopropane **46a**. However, the lower ceiling temperature of the polymer arising from 1,2-vinylic polymerization of **47a–c** (i.e. without ring-opening) preferentially directs the polymerization toward the AF sequence. The kinetics of the



Scheme 16. Energetic diagram in the ring-opening of α-(substituted) cyclopropylmethyl radicals **58a–c**.



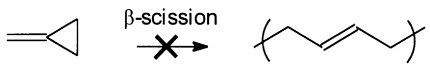
Scheme 17. Equilibrium between radicals **58c** and **59c**.

fragmentation of α-(substituted)cyclopropylmethyl radicals **58a–c** have been studied by Beckwith et al. [117] and Newcomb et al. [118]. Their results are illustrated in Scheme 16, in which only the relative order of the energetic levels have to be considered.

The ring-opening of the simplest radical, cyclopropylmethyl **58a**, the best known of this group, is a very fast radical fragmentation, with a rate constant of 10^7–10^8 s^{-1} at 60°C–80°C. In comparison, the rate of fragmentation of cyclopropylphenylmethyl radical **58c** ($k_{fr} = 1.6 \times 10^6$ s^{-1} at 80°C) appears slower than that of 1-cyclopropylethyl radical **58b** ($k_{fr} = 2–3 \times 10^8$ s^{-1} at 80°C), which is a better model for the poly(vinylcyclopropane) macroradical than cyclopropylmethyl radical **58a**. In the former case, this behavior can be partially explained by a substantial increase of the activation energy for the fragmentation of **58c** upon loss of electron delocalization in the transition state, which cannot be compensated by the conjugation of the double bond with the phenyl ring. The activation energies for the fragmentation reaction of α-(substituted)vinylcyclopropanes have been determined to be ca. 34–39 kJ mol^{-1} for **58a,b** and 61 kJ mol^{-1} for **58c**, and the Arrhenius pre-exponential factors vary slightly in the range $1–10 \times 10^{13}$ s^{-1}. The additional stabilization afforded by the α-methyl and α-phenyl groups over radicals **58b** and **58c** was estimated to be ca. 12 and 46 kJ mol^{-1} [117], respectively, as compared to the cyclopropylmethyl radical **58a**. The equilibrium constants of the fragmentation–cyclization reaction of the cyclopropylphenylmethyl radical **58c** were found to be close to 0.04 and 0.12 at 60°C and 120°C, respectively [117] (Scheme 17).

Another example can be quoted to illustrate the predominance of the stereoelectronic effect. If we consider a hypothetical AF monomer, i.e. methylenecyclopropane, the free radical fragmentation of the corresponding cyclopropyl radical formed after addition on the carbon–carbon unsaturation (yielding an allyl radical) is under the control of stereoelectronic requirements rather than thermodynamic factors (Scheme 18).

The process would be expected to be highly exothermic (ca. 125 kJ mol^{-1}), but the activation energy of the cyclopropyl ring-opening was shown, in gas-phase studies at elevated temperatures, to be very high (ca. 79 kJ mol^{-1}) [119]. The rearrangement of this latter radical does not occur in solution because of its very short life-time. Similarly, the adduct radical resulting from addition on methylenecyclopropane would certainly prefer to react via termination or copolymerization reactions in solution. The fragmentation of the cyclopropyl radical is only observed in solution, when additional features afford further stabilization to the rearranged allyl radical, such as two phenyl groups (Scheme 19 and Sections



Scheme 18. Hypothetical AF polymerization of methylenecyclopropane.

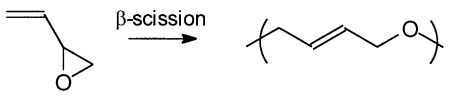
Scheme 19. Allylic stabilization of cyclopropyl radicals by the phenyl groups.

2.1.2 and 2.1.3). However, allylic stabilization is experienced only when the rearrangement has been well developed (according to the Hammond postulate [120]). Such a constraint explains the observed high activation barrier.

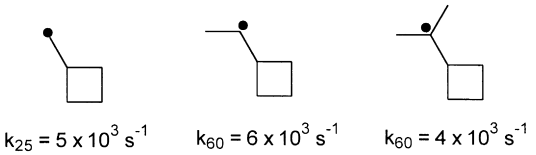
The free radical fragmentation of a 2,3-epoxypropyl radical is similar to the cyclopropylmethyl radical rearrangement [121]. However, it can react in two distinct ways, depending on the substituents on the oxirane ring. Indeed, the kinetic and thermodynamic products may be obtained under reversible conditions. For example, the thermodynamically more stable radical propagates to yield the corresponding polymer units, when unsymmetrical substituted vinyloxiranes are involved in AF polymerization (*note:* the same effect is observed for unsymmetrical substituted cyclopropanes). It can lead to a fast rearrangement (Scheme 6, scission β_1) of the carbon-centered radical to the highly reactive oxygen centered radical (i.e. the reverse of the more common process) [122]. This is a fast exothermic rearrangement [123] which is undoubtedly propelled by the ring-strain relaxation (ca. 115 kJ mol^{-1}) [124] (Scheme 20).

For vinylcycloalkane involving less-strained five- or larger-membered rings, ring-opening is a favorable process, especially when appropriate substituents are present on the ring. Further driving forces for the fragmentation step have to be provided by other factors: scission of a relatively weak C–S bond and loss of sulfur dioxide (e.g. the vinylsulfones **52a–d**, see Section 2.1.6), stabilization of the radical formed (Section 2.1.4) or aromatization of a cyclohexadienyl derivative, as is the case of some spiro derivatives (Section 2.1.3).

Considering the high strain-energy of cyclobutyl rings, both methylenecyclobutane and vinylcyclobutane derivatives have been studied as potential monomers for AF polymerization. However, fragmentation rate constants of cyclobutylcarbinyl radicals have been less investigated than those of their three-membered ring analogs. In most cases, the former are lower than those of the corresponding cyclopropylcarbinyl radicals (ca. four orders of magnitude), in agreement with the smaller ring-strain in the former case (Scheme 21). The exothermic fragmentation of cyclobutylmethyl radical affords only $\Delta H^{o} =$ 16 kJ mol^{-1} [125]. Hiraguri and Endo [126] have shown that methylenecyclobutane and vinylcyclobutane exhibit opposite behaviors. The former monomer undergoes only 1,2-vinylic polymerization [126]. Unlike methylenecyclopropane, the presence of substituents, i.e. Ph, CN, CO_2Me (as a means to stabilize the expected isomer radical resulting from rearrangement), does not afford any improvement in the fragmentation process, because the stabilization is only effective when the rearrangement has been well developed (Scheme 21). Comparatively, substituted vinylcyclobutane (Section 2.1.2.2) afford nearly quantitative AF polymerization [89]. Unlike methylenecyclopropane, the semi-occupied p orbital of the



Scheme 20. Free radical rearrangement of 2,3-epoxypropyl radicals.



Scheme 21. Rate constants for fragmentation of cyclobutylcarbinyl radical derivatives.

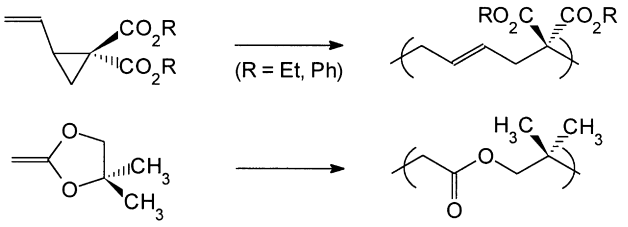
adduct radical formed by radical addition to the unsaturation of methylenecyclobutane cannot overlap with the sp^3 orbital of the adjacent σ C–C linkage of the cyclobutyl ring. Coplanarity (and further β-fragmentation of the bond) can be more easily achieved in the case of vinylcyclobutanes.

2.1.2.2. Substitution pattern The rate of fragmentation of the derivatives of vinylcyclopropyl radicals (ca. 10^5–$10^8\ s^{-1}$) is particularly sensitive to the substitution pattern [116,127,128]. For example, in addition to electronic factors, the presence of two substituents on the same sp^3 carbon leads to the so-called "*geminal*-disubstituent steric effect" and it has been established that the extent of intramolecular rearrangement of the radical polymerization of appropriately substituted functional AF agents, e.g. **46e** and **46h** (Scheme 22), may be greatly enhanced by *geminal* disubstitution [129].

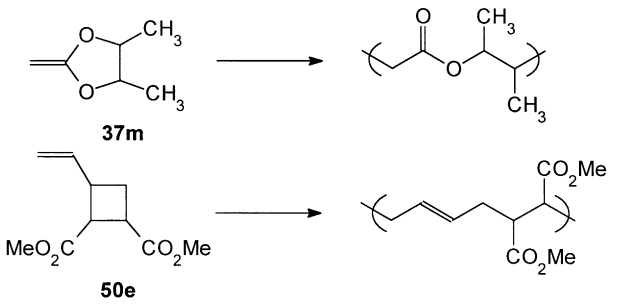
Vinylcyclobutane derivatives bearing *vicinal* substituents on the ring exhibit increased fragmentation rate constants when polymerized, similar to those of non-substituted vinylcyclopropanes [130]. As a result of the incremental strain imparted by two *vicinal* methoxycarbonyl fragments, the rate of ring-opening of the corresponding vinylcyclobutane **50e** was substantially enhanced, with respect to the analogous hydrocarbon system, and the bulk polymerization of vinylcyclobutane afforded 94% fragmentation, at 60°C (Scheme 8) [89]. The fragmentation is also favored, in the case of disubstituted cyclic ketene acetals, by an increased strain effect on the breaking bond (presence of two methyl and phenyl groups in C^4 and C^5 on 2-methylene-1,3-dioxolane derivatives **37m** and **37n**, respectively) (Scheme 23). The stereochemistry of **37m** and **50e** was not specified by the authors, but it is expected that the *Z*-isomer could afford the highest ring-opening rate constant in each case.

2.1.3. Formation of aromatic fragments

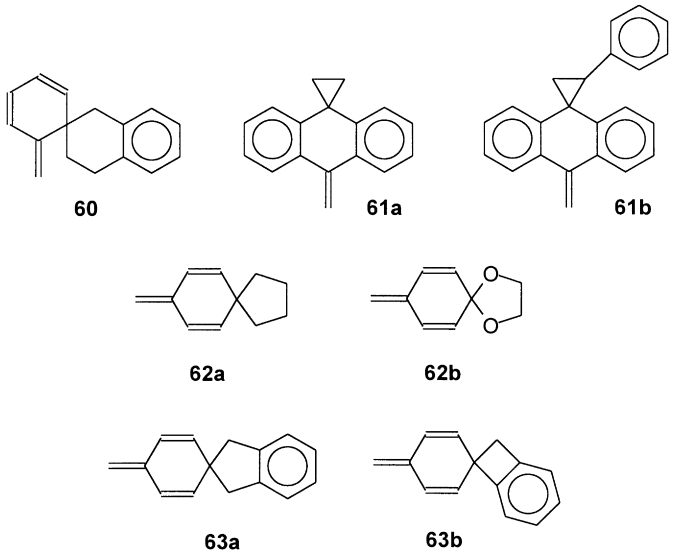
The intramolecular reaction versus copolymerization ratio can be increased by the formation of a conjugated fragment in the AF process [131]. Spiro-di-*o*-xylene **60** [132], 10-methylene-9,10-dihydro-anthryl-9-spirocyclopropane derivatives **61** [133] and various methylenespiro-hexadienes **62** and **63** were used in free radical (co)polymerizations (Scheme 24). They show relatively high reactivity in copolymerization with vinylic monomers.



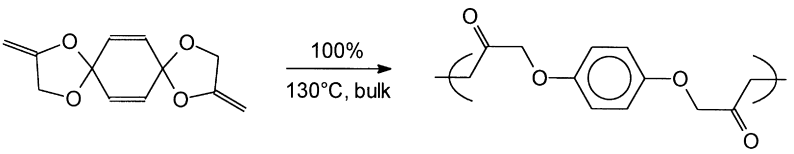
Scheme 22. *gem*-disubstituted steric effect in the polymerization of **46e** and **46h**.



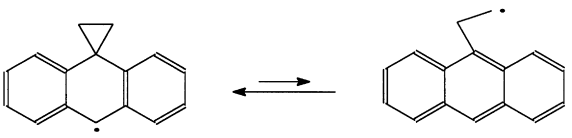
Scheme 23. Effect of vicinal disubstitution on fragmentation efficiency in free radical AF polymerization of vinyl ketene acetals **37m** bearing two methyl groups and vinylcyclobutane **50e** bearing two ethoxycarbonyl fragments.



Scheme 24. Reagents **60–63** designed to allow efficient AF polymerization with aromatization as main driving force for rearrangement.



Scheme 25. AF polymerization of a potentially aromatizable monomer.



64

Scheme 26. Equilibrium in the rearrangement of spiro-10-cyclopropylanthracen-9-yl radical **64** through aromatization.

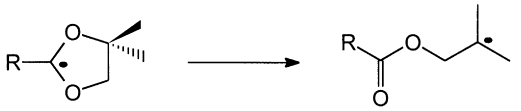
The following AF monomer has also been reported to undergo double ring-opening polymerization at 130°C in the bulk, with no change in volume (Scheme 25) [135]:

The driving force for this process is the strong aromatization which promotes quantitative ring-fragmentation to insert an aromatic fragment into the backbone of the polymer [136]. Like all unimolecular processes, the ring-opening is also favored by an increase of the dilution of the monomer(s), and by a higher temperature [137] (Section 3). Indeed, when stabilization of the starting material is high enough, it disfavors the ring-opening at low temperatures. For instance, the stabilization energy of the spiro-10-cyclopropylanthracen-9-yl radical **64** was estimated to be ca. 100 kJ mol^{-1} [117]. It means that the ring-opening activation energy is high and disfavors the fragmentation process (Scheme 26).

The principle of reversibility of the AF process and the influence of the stability of the adduct radical may also be observed on comparing the rate constants of ring-opening of dioxolan-2-yl, reported by Barclay et al. at 75°C [138] (Scheme 27).

2.1.4. Formation of persistent or stabilized radicals—captodative effect

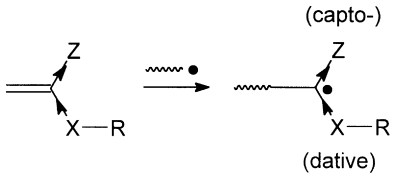
When radicals exhibit self-reaction significantly slower than the diffusion limit, they are said to be "persistent". A C–C bond is generally weakened when substituted by either an electron-donating (e.g. alkoxyl or thioalkoxyl) or an electron-withdrawing fragment (e.g. cyano or carbonyl groups). However, this effect is rather small, ca. 12–20 kJ mol^{-1}. By contrast, a synergistic effect occurs when both types of substituents are located on the carbon bearing the radical center. In this case, the radical stabilization is much greater than one could expect from the sum of the effects of the two separate fragments. Such a supplementary stabilization is usually called the "captodative" effect (i.e. the electron-withdrawing and -donating are the "capto" and the "dative" groups, respectively) [103]. It seems that such a "captodative" effect is a kinetic effect (i.e. through the transition state) rather than a thermodynamic stabilization of radicals by this effect. In that sense, this term has to be differentiated from "stabilized". For instance, the benzyl radical is not a persistent species. It implies a significant measure of resonance stabilization and its dimerization is mainly diffusion-controlled. The relatively high radical



$R = CH_3$ $k_{(75°C)} = 7.6 \times 10^3\ s^{-1}$

$R = H$ $k_{(75°C)} = 1.0 \times 10^3\ s^{-1}$

Scheme 27. Rate constants in the fragmentation of dioxolan-2-yl-type radicals.



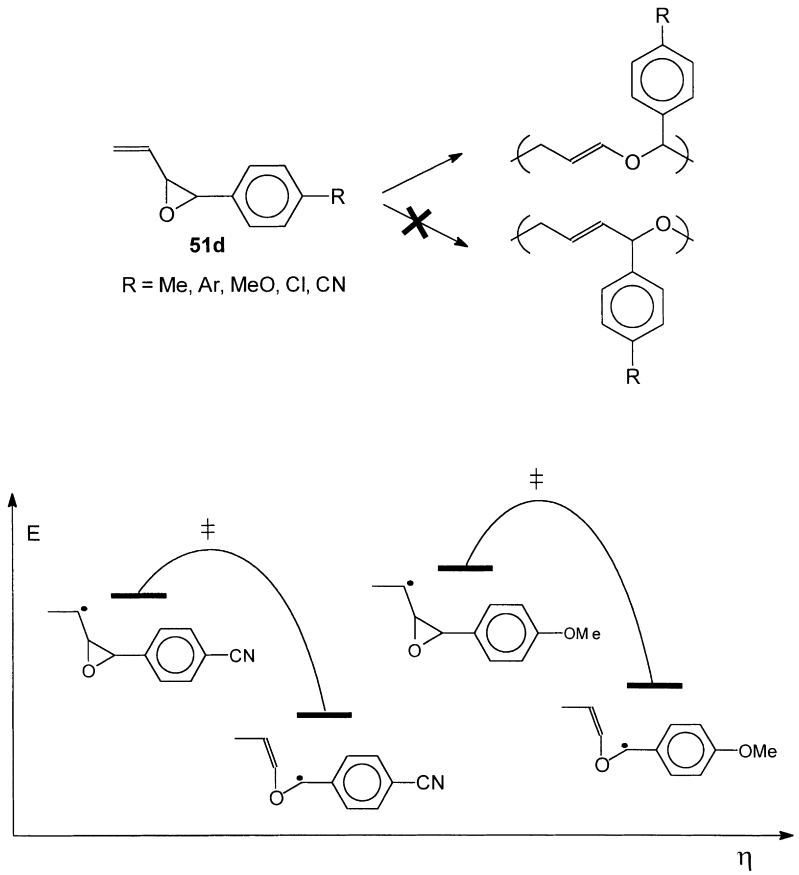
Scheme 28. Capto-dative effect on radicals formed through the addition step.

concentrations which may be maintained in solution reflect the persistence of a radical species. The chemoselectivity for reactions, in which such radicals are intermediates, can be strongly influenced and more high efficiency can be obtained. These concepts have prompted extensive studies in radical chemistry, particularly in the field of the chain-growth control of macroradicals, recently reviewed by the author [139]. AF processes were investigated through the use of reagents bearing captodative substituents located either on the unsaturation or on the leaving fragment, in order to stabilize the formed radicals and to increase the fragmentation efficiency versus propagation.

2.1.4.1. Radicals formed through addition Various ethylenes with 1,1-captodative substituents have been investigated as new AF agents (Scheme 28) [140]. In the case of cyclic α-alkoxyacrylates [41], the rate of their AF polymerization appears to be slower than for the corresponding exomethylene cyclic ketene acetals **37**. In the former case, a captodative radical is produced, which decreases the efficiency of the propagation reaction. However, the corresponding six-membered ring systems afford higher fragmentation efficiencies than in the case of the corresponding 4-methylene-1,3-dioxolane, particularly when the formed radical is stabilized by substituents (e.g. CH_3, Ph). No β-scission yielding acyl radical propagating species was observed, which is probably due to a higher bond strength of the bond α to the carbonyl group. The presence of a radical-stabilizing group, i.e. phenyl or *p*-(substituted)phenyl, on vinylcyclopropane [85,141] is also a means to increase the conversion [141], when compared to results obtained with non-activated compound **46a**. For instance, vinylcyclopropanes **47a–c**, bearing an aromatic fragment on the unsaturation were radically polymerized by an exclusive AF process through the formation of an intermediary benzylic radical [142,143].

2.1.4.2. Radicals formed by fragmentation The fragmentation is always favored by the presence of substituents (e.g. Ph, CO_2R, CN, Cl) which stabilize the newly formed radical. For example, the (co)polymerization of cyclic ketene acetals **37g** gave quantitative ring-opening, the additional driving force for the fragmentation being provided by the formation of benzylic radical (in Section 2.1.2, we noted that its parent **37a** does not afford efficient fragmentation under the same conditions). The same effect may also be observed in the AF polymerization of 2-vinyl cyclic ethers **44**. The extents of fragmentation in the polymerization of **44a**, compared to **44c**, were ca. 5% and 50%, respectively, in agreement with the presence or not of a phenyl group in α to the oxygen on the cycle [144]. Endo et al. have estimated the relative AF polymerization rates of cyclic ketene acetals **37** involving quantitative fragmentation. It was shown that ketene acetals with radical stabilizing groups polymerize more slowly than their non-substituted homologues. The relative polymerization rates are noted between parentheses as follows: **37d** (1.00) $>$ **37f** (0.69) $\gg$ **37g** (0.022) $>$ **37h** (0.020) [40].

The AF polymerization of the unsubstituted vinylcyclopropane **46a** gives polymers containing more than 80% of units provided by the AF process [145]. The presence of radical stabilizing groups on the

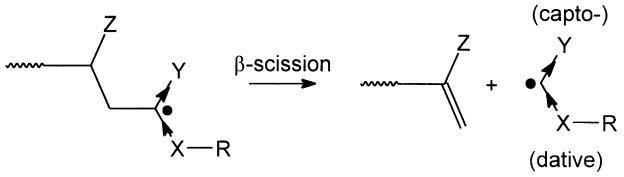


Scheme 29. AF polymerization of *p*-substituted-2-phenyl-3-vinyloxiranes **51d**.

cyclopropyl ring accelerates strongly the rate of ring-opening reactions through a stabilizing effect in the transition state. More than three orders of magnitude are often observed between the rate constants for ring-opening of poly(vinylcyclopropyl) radicals bearing a phenyl substituent (**46i** [186]) or electron-withdrawing groups (chloro: **46b** [175]; dichloro: **46c** [177]; ester and/or cyano: **46d** [178–180], **46e**,**f** [181–184], **46g**,**h** [183,185]; carbonate moieties: **46k** [187]) or both (**46j** [180]), and their parent, i.e. cyclopropylmethyl radical. For example, the rate constants for ring-opening of a mixture of *cis*- and *trans*-2-(ethoxycarbonyl) cyclopropylcarbinyl radicals were estimated to be $> 5 \times 10^{10}\ s^{-1}$ at 60°C.

The AF polymerization of vinyloxiranes **51** exhibits similar properties. When an aryl group is present on the ring of the oxiranylmethyl radical, a selective cleavage (Scheme 6, scission β_2) of the carbon–carbon bond of the oxirane ring affords the radical **65**, leading to the introduction of a vinyl ether microstructure unit **66** in the backbone of the polymer chain. The aryl substituent on the oxirane acts as a radical stabilizing group in the fragmentation of the intermediate radical **67** [146,147]. In the case of *para*-substituted-2-phenyl-3-vinyloxirane derivatives **51d** (Scheme 29), the nature of the *p*-substituent R on the phenyl ring is also a factor affecting the extent of fragmentation in the polymerization [146,147].

AF reagents bearing capto-dative substituents on the leaving fragment were proposed recently for



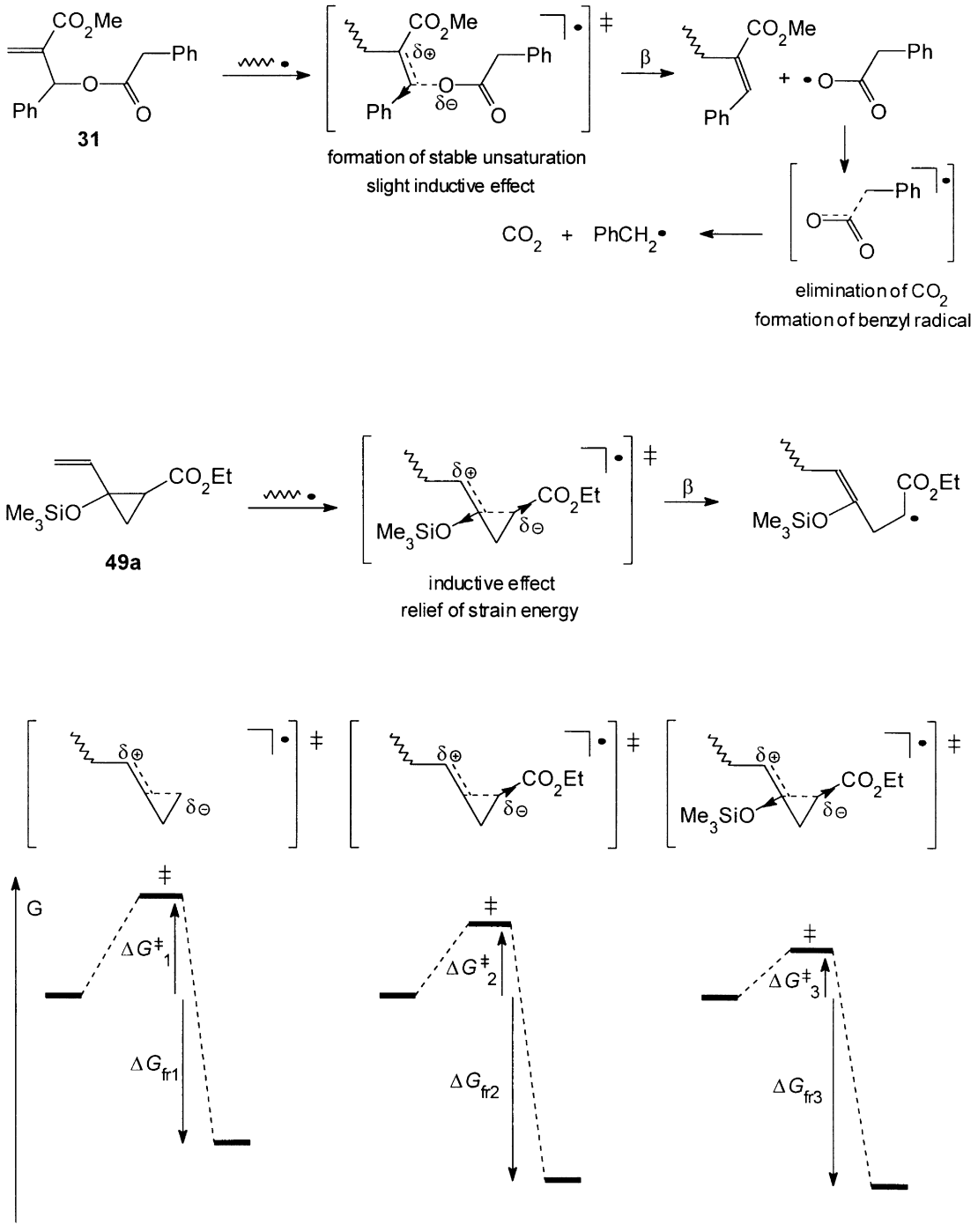
Scheme 30. Capto-dative effect on radical formed by fragmentation.

radical polymerization, the stabilized captodative radicals being ejected instead of the usual heteroatom-containing substituents. As previously mentioned, radicals formed on a carbon bearing both electron-donor (dative) and electron-acceptor (captive) substituents are much more stabilized than those bearing only one of them. In such systems, the degree of efficiency of these AF agents depends on the involved captodative substituents [103,148]. Softer heteroatoms like sulfur stabilized the radicals better than the alkoxyl groups (Scheme 30). The reactivity of 1,1-disubstituted ethylene bearing captodative groups towards radicals and the stability of the resulting radicals were reported by Viehe et al. [149] and Nair et al. [150].

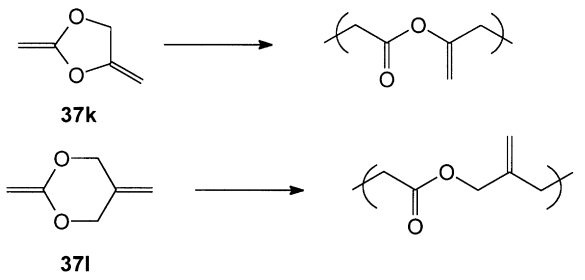
2.1.5. Formation of stable carbonyl function or double bond

The fragmentation process [29] can be greatly facilitated by further stabilization of the newly formed olefin upon introduction of a fragment involving a conjugation (i.e. phenyl: **31**, and trimethylsilyloxyl: **49a**) at the allylic position of the AF agent (Scheme 31). In the case of **49a**, the AF polymerization occurs exclusively by selective cleavage of the C–C bond substituted by both the ester and the trimethylsiloxyl groups. According to the transition state, located early in the reaction coordinate of the process (Scheme 31), the inductive electron-withdrawing effect of these two groups contributes to an important part in the efficiency and selectivity of the fragmentation.

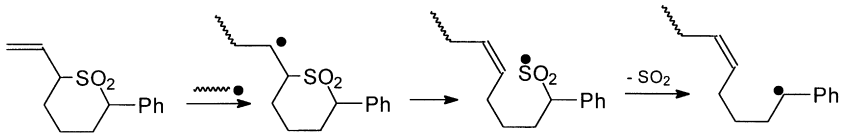
The formation of a strong carbonyl function also represents one of the main driving forces for the fragmentation step in the polymerization of cyclic ketene acetals **37**, to afford polyesters. The introduction of amide or thioester functions in the polymer backbone may also be obtained by selective cleavage of the C–O bond in the radical ring-opening polymerization of nitrogen and sulfur analogs of 2-methylene-1,3-dioxolane, i.e. **37i** and **37j**, respectively. The greater bond strength of C=O (mean value of $\Delta H^{\circ}_{fr} = 720–760\ kJ\ mol^{-1}$, at 25°C) versus C=N- (ca. $650–600\ kJ\ mol^{-1}$) or C=S (ca. $550\ kJ\ mol^{-1}$, from CS_2) double bonds may explain the specificity of the fragmentation [151]. Polymerization of **37i** and **37j**, respectively, afforded a quantitative and a limited fragmentation efficiency. The amide fragment is as stable as the ester group arising from the evolution of **37a**, whereas the thioester function is substantially less stable than the ordinary ester function, and it therefore retards the extent of fragmentation. Comparatively, the polymerization of the corresponding cyclic 2-methylene-1,3-dithiane does not undergo cleavage at the C–S bond, even though the bond strength of C=S is weaker than that of C=O. Such a behavior is due to difficulties in achieving the accurate configuration for orbital overlap in the transition state (i.e. stereoelectronic effects, see Section 2.1.2.1). Cyclic ketene acetals, 2,4-dimethylene-1,3-dioxolane **37k** and 2,5-dimethylene-1,3-dioxane **37l**, respectively underwent (under the same conditions: 120°C, DMF) [152] quantitative AF polymerization and radical polymerization with both AF and copolymerization (Scheme 32). In the latter case, the carbonyl function is formed in parallel with the formation of stabilized radicals.



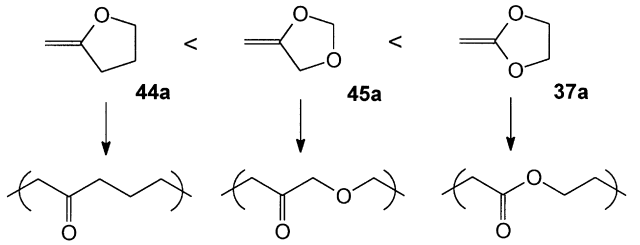
Scheme 31. Examples of AF transfer agent and monomer designed to allow efficient fragmentation step.



Scheme 32. Free radical polymerization of cyclic ketene acetals **37k** and **37l**.



Scheme 33. Elimination of sulfur dioxide in the AF polymerization of 2-vinyl cyclic sulfone **52d**.



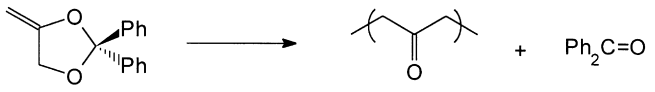
Scheme 34. Comparison of the relative rates of fragmentation of 2-methylene tetrahydrofuran and 4- or 2-methylene-1,3-dioxolane, i.e. **44a**, **45a** and **37a**, respectively.

2.1.6. Elimination of a molecule

The efficient free radical AF polymerization of strained 2-vinyl cyclic sulfones **52a–d** [153] was reported by Cho et al. [154] to be particularly selective (Scheme 6, scission β_2). Such a behavior is favored by the elimination of gaseous SO_2 (Scheme 33).

Exomethylene cyclic vinyl ethers **44a–e** (i.e. 2-methylenetetrahydrofuran **44a** and related compounds) have also been shown to undergo free radical AF polymerization at 120°C: ketone functions are introduced into the backbone of radical addition polymers. The extent of the AF process was shown to be less important than that of the corresponding 2- or 4-methylene-1,3-dioxolane derivatives, i.e. **37** and **45**. Such a result is explained by a slightly lower stability of a ketone function as compared to an ester function (Section 2.1.5), or by an easier possibility to adopt the required conformation for fragmentation (i.e. stereoelectronic constraints, see Section 2.1.2.1) when two oxygen atoms are present on the ring (Scheme 34).

The 4-methylene-1,3-dioxolane **45a–e** derivatives undergo a double fragmentation evolution (ca. ring-opening and ketone elimination, Scheme 6), which incorporate carbonyl functions in the backbone of the resulting polymer. The occurrence of the second β-scission step with elimination of a ketone molecule (Scheme 6, scission β_3) is the main driving force of the reaction. It depends on the substituents



45b

Scheme 35. AF polymerization of 2,2-diphenyl-4-methylene-1,3-dioxolane **45b** with elimination of benzophenone.

located at the 2-position and is also controlled by the reaction conditions. The thermally initiated radical polymerization of 2-phenyl-4-methylene-1,3-dioxolane **45c** and related compounds **45d,e** or its photopolymerization performed at temperature higher than 80°C evidenced structures originating from mixed polymerization modes (addition, AF and even addition–fragmentation–elimination polymerization) [155–157,159]. The monosubstituted 2-phenyl derivative **45c** not only afforded incomplete ring-opening (73% at 120°C), but also partial elimination of benzaldehyde (36%). At $T < 30$°C and under UV initiation, quantitative ring-opening was observed with no elimination. The 2-phenyl-2-methyl derivative **45h** gave only 23% of ring-opening at 120°C, followed by 100% elimination of acetophenone, under the same conditions. The bulk polymerization of the 2,2-diphenyl-4-methylene-1,3-dioxolane **45b** at 120°C, reported by Endo [158,159], afforded the polyketone quantitatively with subsequent elimination of benzophenone (Scheme 35).

In the case of 2,2-diaryl-4-methylene-1,3-dioxolane **45f**, Endo et al. [66] showed that the polymer yields increased with the electron-donating character of the *para* substituents on the phenyl rings. Such a phenomenon was related to a lowering of the activation energy of propagation promoted by electron-donating groups in the transition state [83,84].

2.2. Factors controlling the unsaturation reactivity

This section is concerned with the polar and steric factors controlling the unsaturation reactivity, it is hoped that the reader will acquire an understanding of the addition process, particularly as it applies to polymerization reactions. It will be necessary to refer to the addition to usual alkenes, but this will only be done in order to explain the chemistry involved in AF reactions, because much work of a fundamental nature has been carried out with classical monomers.

It may often be desirable to estimate the ease of an elementary radical addition to a π-system from the difference between the strength of bonds being broken and formed. However, the outcome of a radical addition cannot be determined accurately through the influence of a single factor. Resonance, polar, and steric effects also direct the radical addition to the olefins, in determining the orientation (i.e. regioselectivity) and the rate of the reaction. For example, styrene is a more reactive monomer than vinyl acetate but the polystyryl radical is less reactive than the poly(vinyl acetate) radical, the latter being less stable than the former. These effects are often so pronounced in radical addition that they usually determine the outcome of the reaction and outweigh any simple thermochemical analysis. The influence of polar and steric factors has been used rather recently to rationalize the copolymerization reactivities of vinylic monomers and wewill see that it can also explain to a large extent most of the chain transfer constants obtained with AF transfer agents and, more generally, the reactivity of all AF reagents. In the following sections, the determination of the outcome of radical addition will be based on a comparison of resonance, polar, and steric factors. The guidelines mentioned in the following are based on a set of simple empirical principles suggested in the last fifteen years by Tedder [160,161], Curran [162],

Beckwith [163], and Giese [164]. They allow quantitative prediction of radical addition reactions and are adapted in the case of AF agents:

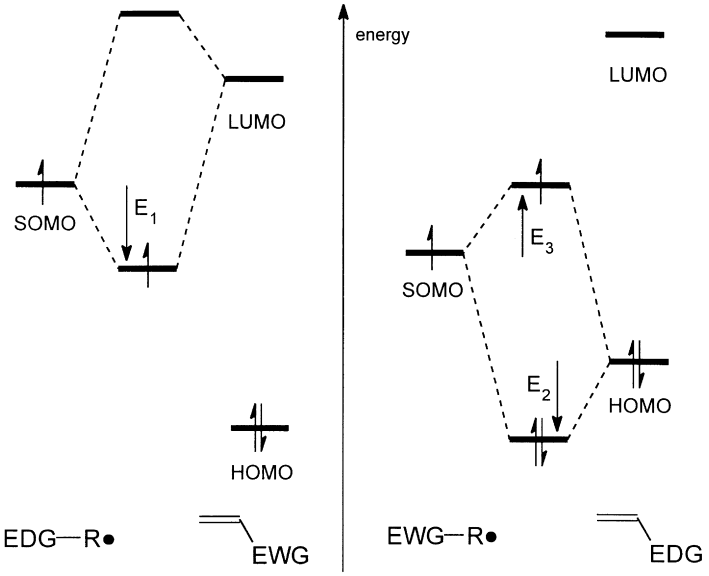
- Steric effects, i.e. the degree of steric compression observed upon forming a new bond, appeared as a major factor determining the occurrence and the regioselectivity of the addition step. As in the case of usual monomers, the 1,1-disubstituted AF agents which have been studied till date always exhibit preferential addition to the unsubstituted end of the unsaturation [2]. The steric hindrance induced by the formation of the new bond represents the major factor which directs the regioselectivity of the addition reaction. Steric effects are overridden by polar factors when the former are small or mutually opposed. In spite of the general predominance of head-to-tail addition in most radical addition polymerization, some side-reactions may occur, leading to imperfections (e.g. head-to-head addition) with a probability depending on the nature of the compound involved. These aspects have been recently detailed by Moad and Solomon in the case of the polymerization of vinylic monomer [1]. In the case of AF agents, these investigations leave little room for doubt that the addition step should proceed through head-to-tail addition.
- It is also considered that the rate of addition at the remote end of the double bond can be enhanced by the overlap between the half-filled atomic orbital of the incipient radical center and the substituents with π-orbitals (e.g. $CH{=}CH_2$, Ph, CO_2R, CN). Substituents with non-bonding pairs of electrons (e.g. F, Cl, OR) have only very small resonance effects but a high polar contribution through inductive electron-withdrawing effects. Reactivity and selectivity of radical reactions can be described by specific frontier molecular orbital interactions, because radical additions on AF agents are exothermic and their transition states are located early on the reaction coordinates. The geometry of orbitals in the transition states resembles more the starting radicals than their rearranged isomers. In this case, the delocalization of the unpaired electron in the adduct radical directs the reactivity of the process to a fair extent.
- Another very important transition state effect can be exemplified by consideration of the favored addition of electrophilic radicals on styrene as compared to their addition on acrylates. One can rationalize this behavior in terms of a polar effect, i.e. partial charge separation, stabilizing the transition state. The overall rate of addition of nucleophilic and electrophilic radicals is dramatically enhanced by the polarity of the double bond of the AF agent (e.g. the presence of electron-withdrawing or -donating substituents, respectively). It is the case, for example, in a polymerization reaction in the presence of an electron-rich reagent, when the growing macroradical is rendered relatively electrophilic by an electron-withdrawing substituent. Its tendency to add to another electron-deficient monomer (i.e. acrylonitrile) is thereby diminished when compared to a simple alkyl radical, whereas its attack on the unsaturation to the electron-rich AF agent is easier.

A non-negligible role influencing the outcome of the reaction is devoted to thermodynamic factors solely when kinetic parameters (i.e. polar and steric effects) are more or less evenly balanced. Thus, one of the main thermodynamic driving effects controlling the outcome of radical addition reactions is the stability of the formed radical. Such a stability can be due to the radical itself or provided by a substantial delocalization of the radical into a π-system. We have seen before that the presence of substituent at the radical center which stabilizes it is not the sole explanation for preferential tail addition. However, in the absence of steric effects, the relative stability of the radicals formed may be used to compare the various rate constants obtained in the addition of radicals to olefins. By contrast,

the stabilization of the incipient radical center [165,166] does not affect much the rate and the specificity of the reaction. In this review, the factors controlling the unsaturation reactivity of AF agents (i.e. factors influencing rates and regioselectivity of addition) are discussed in detail, using the current knowledge and data reported earlier.

2.2.1. Polar and steric effects

A fast AF reaction requires not only a labile bond, but also a sufficiently high reactivity of the unsaturation. To illustrate this requirement, it appears that the reactivity of cyclic ketene acetals **37** in copolymerization is generally rather low, in spite of a quantitative free radical AF homopolymerization. On the contrary, cyclic α-alkoxyacrylates **40** exhibit high reactivities in both homo- and copolymerization with styrene and (meth)acrylates [167], even though the extent of fragmentation depends on the reaction conditions and the substituents on the radicals formed. Polar effects are the main factors which control the overall reactivity and the degree of regiospecificity (i.e. addition to the unsubstituted methylene carbon of 1-mono or 1,1-disubstituted double bond in the monomer) in radical addition to a double bond bearing activating groups. Inductive and/or mesomeric electron-withdrawing groups (i.e. halogen, CO_2R, CN, SO_2Ph) enhance the overall reactivity towards nucleophilic radicals (i.e. alkyl radicals R·) and reduce reactivity towards electrophilic radicals, whereas electron-donating substituents (i.e. alkyl, OR) exhibit the opposite effect. The electron-withdrawing effect lowers the energy of the lowest unoccupied molecular orbital (LUMO) of the olefin whereas the electron-donating effect increases the energy of the highest occupied molecular orbital (HOMO) of the olefin, according to the frontier molecular orbital theories. In each case, a smaller energy difference (ΔE) between the LUMO (or the HOMO) and the SOMO of radical R· is then obtained. The rate of addition is increased [168], the adduct radical being also influenced by the presence of an electron-withdrawing (left-hand side diagram) or



Scheme 36. Frontier molecular orbital interactions of the SOMO of an activated radical with the LUMO or the HOMO of an unsaturated molecule.

donating group (right-hand side), respectively (Scheme 36). Both interactions are bonding, the stabilization energy of the former being E_1 and the latter $2E_2 - E_3$.

Activating groups on unsaturation of AF agents are generally either alkoxycarbonyl, alkylcarbonyl, amidocarbonyl, cyano or phenyl groups (Table 1, fragments Y and Y′). They can also be cyclic (**14**) or acyclic (**9**, **32–36**) diene fragments or cyclic thiovinyl moieties (**15**). The nature of the site of addition is nearly always a methylene fragment on AF monomers. In the case of AF transfer agents, reagents bearing terminal carbon–carbon double bond are mainly reported, but thiocarbonyl fragment and substituted methylene (PhCH and CH_3CH) have also been studied (Table 1, fragments X).

The presence of substituents directly bound to the reaction center of an AF reagent, in α- or β-position on the double bond, causes important steric and polar effects and controls the reactivity toward an attacking radical, depending on the nature of substituents involved. Although the importance of polar effects in the reaction of an AF agent bearing a mono-, a di- or even a trisubstituted unsaturation can be anticipated, the significance of steric hindrance of substituents in AF processes is always difficult to estimate. Most of the steric effects are identified once the reaction has been carried out.

2.2.1.1. Substitution on vinylic α-carbon The purpose of this section is to summarize the effects of functional α-alkyl groups involved in the reactivity of AF reagents in free radical polymerization. We observe that there is not much work done concerning the effect of series of alkyl groups in the α-position of α,β-unsaturated AF agents upon addition behavior. Most studies have been performed on α-acrylic esters. In the following, the most relevant AF agents are compared to the corresponding α-substituted monomers (Table 4).

Polar and steric parameters of both the carbon–carbon double bond and the corresponding polymeric radical are particularly influenced by the introduction of a substituent in α position in the vinyl monomer. Generally, the fragmentation of strained or non-strained linkages is favored when the latter are located onto the AF agent in such a way to reduce the inherent reactivity of the adduct radical toward propagation, the steric inhibition making the intermolecular reaction less favorable. Following this point of view, the study of polar and steric factors influencing the reactivity of various alkyl 2-(substituted) methylpropenoates and related compounds versus diverse vinylic monomers (i.e. St, MMA, BA, MA) can be exemplified by comparison of their cross-propagation rate constants k_{12} with an estimation of transfer rate constant k_{tr} defined as: $k_{tr} = C_{tr} \times k_{11}$ (Table 4 and Scheme 1).

Regarless of the type of monomer used, radical addition on methyl 2-ethylpropenoate at the substituted carbon is strongly retarded, while the rate of addition to the other end is slightly affected by the steric hindrance of a primary α-substituent, and much more so in the case of very bulky groups (secondary and tertiary carbons). Generally, primary alkyl substitutions of α-hydrogen in methyl acrylate have little or no influence on the monomer reactivity ratios in copolymerizations whereas secondary-alkyl substitutions results in an important change of the overall (co)polymerization rates, according to the nature of α-alkyl groups. α-*iso*-propyl- and α-*sec*-butylacrylate exhibit relative reactivities ($1/r_1$) toward polystyryl radical (styrene is the monomer *1*) close to 0.54 and 0.44, respectively, and r_2 values close to zero (Table 4, entries 18–19). The slightly higher reactivity of MMA compared with methyl acrylate versus St (r_1 = ca. 0.5 and 0.8, respectively) may be accounted for on the basis of hyperconjugation of the α-methyl group with the double bond. Of course, even if a hyperconjugation effect is involved in α-higher-alkylacrylates to a certain extent, it should be noted that there is another dominant influential effect, i.e. steric interaction, of α-alkyl substituents in the case of such acrylates. Thus, it seems reasonable to consider that the difference in the relative reactivities ($1/r_1$) of methyl α-alkylacrylates

Table 4
Rate constants[a] for (co)polymerization of St, MMA, BA and MA[b] in the presence of various α-substituted compounds[c] at 60°C

Entry	(M_1)	(M_2)	k_{12} (l mol^{-1} s^{-1})	k_{21} (l mol^{-1} s^{-1})	Ref.
1	St	St	187	187	[169]
2	St	α-MeSt	170 ± 5	440 ± 150	[169]
3	St	**21a**	550	/	[27]
4	St	**21b**	150	/	[32]
5	St	**21c–g**	130–180	/	[28]
6	St	α-MeOSt	65–90	2670	[170]
7	St	**13a**	50	/	[21]
8	St	MMA	630	1110	[169]
9	St	α-EtMA	250	950	[174]
10	St	α-*n*PrMA	230	900	[174]
11	St	α-*n*BuMA	230	910	[174]
12	St	α-$ClCH_2EA$	105	1170	[171]
13	St	**18a**	440	/	[26,27]
14	St	**18c**	180–220	/	[28,29]
15	St	**18d,e**	215–320	/	[28]
16	St	**18f,h**	785–1270	/	[27]
17	St	**18I**	370	/	[29]
18	St	α-*iso*PrMA	100	5195	[174]
19	St	α-*sec*BuMA	80	46750	[174]
20	St	**1, 5, 7a**	160–190	/	[9,12,16]
21	St	α-*iso*BuMA	190	925	[174]
22	St	**29a,b**	40–100	/	[29]
23	St	α-BzMA	330	1070	[169]
24	St	**30**	350	/	[29]
25	St	α-$HOCH_2MA$	400	330	[172,173]
26	St	α-$PhOCH_2MA$	320	1100	[174]
27	St	α-$BzOCH_2MA$	690	520	[175]
28	St	α-$BuOCH_2MA$	420	850	[176]
29	St	**2a**	310	/	[10]
30	St	α-$MeCO_2CH_2EA$	550	980	[177]
31	St	α-$PhCO_2CH_2EA$	620	700	[178]
32	St	**31**	100	/	[29]
33	St	α-MeOMA	160 ± 10	325–400	[179]
34	St	**13c**	10	/	[22]
35	St	MAA	2790–4670	310	[180]
36	St	**19a,b**	237–338	/	[28]
37	St	MAAm	135	150–400	[169]
38	St	**13d**	30	/	[22]
39	St	AN	600 ± 30	1100	[169]
40	St	α-MeAN	550	890	[169]
41	St	**20b**	355	/	[32]
42	St	α-MeOAN	350 ± 40	600 ± 100	[169]
43	St	**13b**	10	/	[22]

Table 4 (*continued*)

Entry	(M_1)	(M_2)	k_{12} (l mol^{-1} s^{-1})	k_{21} (l mol^{-1} s^{-1})	Ref.
44	St	VA	0.003	3–20 × 10^3	[169]
46	St	EC	120	2340	[169]
47	St	**4, 22**	20–70	/	[11]
48	MMA	MMA	705	705	[169]
49	MMA	α-BzMA	300		[169]
50	MMA	**5, 7**	60–100	/	[12,14,16]
51	MMA	**2a**	440	/	[10]
52	MMA	MAA	1260–3370		[169]
53	MMA	**19a,b**	190–450	/	[28]
54	MMA	AN	530 ± 20		[169]
55	MMA	α-MeAN	850		[169]
56	MMA	**20a**	1560	/	[31]
57	MMA	**20b**	950	/	[32]
58	MMA	St	1110		[169]
59	MMA	α-MeSt	1280–1680	1380	[169]
60	MMA	**21a**	1600	/	[27]
61	MMA	**21I**	1330	/	[27]
62	MMA	**21b–g**	630–870	/	[28,32]
63	MMA	α-MeOSt	280 ± 40	high	[169]
64	MMA	**13a–c**	70–260	/	[169]
65	MMA	MAAm	430–510		[169]
66	MMA	**13d**	330	/	[22]
67	MMA	Butadiene	3200 ± 1000	940–1170	[169]
68	MMA	PD	1640 ± 40	1760 ± 80	[181]
69	MMA	Isoprene	4700 ± 1000	810–1130	[169]
70	MMA	**32a, 34**	2250 ± 150	/	[34]
71	MMA	**33a**	710 ± 60	/	[29,36]
72	MMA	**9a,b**	2250	/	[19]
73	BA	BA	2000	2000	[169]
74	BA	MAA	6450	1600	[182]
75	BA	**19a**	3000	/	[28]
76	BA	MMA	18 200	700–2200	[169]
77	BA	**1**	1600	/	[9]
78	BA	**2b**	2680	/	[10]
79	BA	**5**	1260–2040	/	[13,14]
80	BA	**7a,b**	3900 ± 100	/	[16]
81	BA	**18d**	2560	/	[28]
82	BA	**18f,g,j,k**	3400–4600	/	[27,28,30]
83	BA	St	250	950	[169]
84	BA	AN	1950 ± 150	1350 ± 150	[169]
85	BA	**20a**	6000	/	[31]
86	BA	PD	4760	11140 ± 600	[169]
87	BA	**9a,b**	10 500	/	[19]
88	MA	MA	11 700	11700	[169]

Table 4 (*continued*)

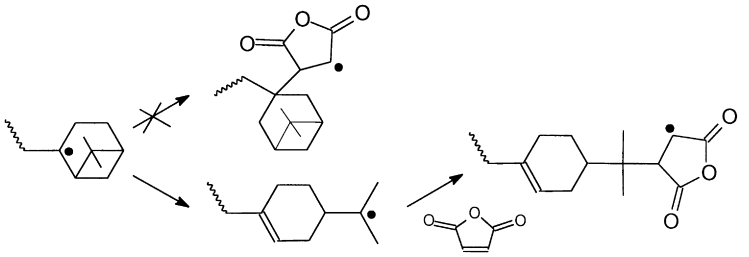
Entry	(M_1)	(M_2)	k_{12} (l mol^{-1} s^{-1})	k_{21} (l mol^{-1} s^{-1})	Ref.
89	MA	MMA	53 250	9900	[183
90	MA	**18a**	34 000	/	[26
91	MA	St	1.3×10^5	$2–3 \times 10^4$	[169]
92	MA	α-MeOSt	69 000	very high	[169]
93	MA	**13a**	67 000	/	[21]
94	MA[d]	MAAm	29 200		[169]
95	MA	**13d**	13 000	/	[169]

[a] Reactivity ratios referred to Ref. [169] are obtained from an average of the most relevant data available.
[b] The (co)polymerization rate constants were determined according to $k_{12} = k_{11}/r_1$ or $k_{21} = k_{22}/r_2$.
[c] In the case of AF transfer agents, k_{12} were estimated from the corresponding chain transfer constants.
[d] Reactivity ratio taken from AN/MAAm copolymerization as an approximation.

toward styrene radical mainly results from the steric factor of the α-substituents, as the difference in polarity between various alkyl groups is very small. Alkyl groups have more or less electron-releasing character (σ^+: from Me = 0.00 to *sec*-Bu = − 0.21). Reactivity ratios and *Q*, *e*-values of α-*n*-alkylacrylates, except methacrylates but including α-*iso*-butylacrylates, appeared similar to those determined for their unsubstituted homologue, i.e. methyl acrylate. Concerning methyl α-benzylacrylate, its copolymerization parameters (versus St) were found to be intermediate between those for methyl acrylate and methyl methacrylate. In such a case, the deviation will be partially attributed to the slight electron-withdrawing effect of benzyl group (polar substituent constant, $\sigma^+ = 0.215$, facilitating the reaction of the monomer with styrene ($e = -0.8$).

As a result of the interpositioning of a unique methylene (or substituted methylene) group between the double bond of α-$BzOCH_2MA$ (entry 27) and the alkoxyl group in the α-substituent, the higher reactivity of α-$BzOCH_2MA$ toward the PS· macroradical ($k_{12} = 1250$ l mol^{-1} s^{-1}) can be ascribed to a polar effect due to the electronic influence of the electronegative oxygen atom in the α-substituent. As a first approximation, one would expect a similar effect in the reactivity of PS· radicals toward **2a** and **5a**. However, the outcome of the addition is rather controlled by steric factor, the addition rate onto the unsaturation of **1**, **5** and **7** (entry 20: $k_{12} = 160–190$ l mol^{-1} s^{-1}) being even more depressed than in the case of **2a** (entry 29: $k_{12} = 310$ l mol^{-1} s^{-1}). This is due to the presence of a methyl group in allylic position of the double bond. These latter results are very close to those reported for α-*iso*PrMA and α-*sec*BuMA (entries 18, 19). In the case of the reaction of **31** toward PS· macroradicals, k_{12} is five-to-six fold smaller as compared to the cross-propagation rate constant of PS· on α-$MeCO_2CH_2EA$ and α-$PhCO_2CH_2EA$ (ca. 550–620 l mol^{-1} s^{-1}: entries 30–31), the outcome of this addition step being controlled mainly by the steric hindrance of the α-secondary substituents.

If we compare the copolymerizability of PMMA· and poly(MMA)-α-$BzOCH_2MA$· radicals toward styrene (entries 8 and 27: $k_{12} = 1110$ and 520 l mol^{-1} s^{-1}, respectively), the latter one is depressed by steric hindrance, even though the electronic influence of the oxygen atom is also operative in that case. It is the reason why synergetic effect between polar and steric factors of α-substituent have to be considered to understand the reactivity of the unsaturation of α-substituted AF monomer or transfer agent, as compared to that of MMA towards polystyryl radicals.



Scheme 37. Competition of the adduct radical formed on -pinene between fragmentation and addition on maleic anhydride.

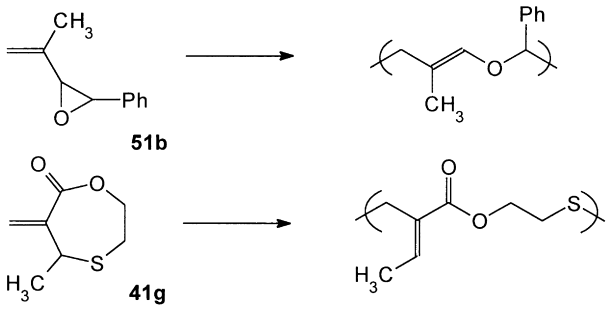
Similarly, the lower reactivity of PMMA-α-$BzOCH_2MA\cdot$ macroradical toward **2a** and **5a** can be related to the electronic and steric effects of the α-substituent.

The reactivity of **13b** and **13c** versus PS· is dramatically depressed ($k_{12} = 10$ l mol^{-1} s^{-1}, entries 34 and 43) in comparison with the copolymerization of St with α-MeOAN and with α-MeOMA ($k_{12} = 350 \pm 40$ and 160 ± 10 l mol^{-1} s^{-1}, entries 42 and 33, respectively). Comparatively, the reactivity of **13a** is rather close to that of α-MeOSt ($k_{12} = 65$–90 l mol^{-1} s^{-1}, entry 6). It is thus difficult to conclude on the common role of the additional steric hindrance to explain the difference between expected and measured values. The occurrence of a degradative chain transfer could explain such a behavior.

The rate constants of addition of **21b–g** ($k_{12} = 130$–180 l mol^{-1} s^{-1}, entries 4,5) are similar to the rate constant of copolymerization of PS· radical on α-MeSt ($k_{12} = 170$ l mol^{-1} s^{-1}, entry 2: value slightly lower than the rate constant of propagation of styrene): either the kinetic parameters (i.e. polar and steric effects) exhibit no effect or they are more or less evenly balanced. On the contrary, the higher reactivity of **21a** toward PS· macroradical ($k_{12} = 550$ l mol^{-1} s^{-1}, entry 3) could be ascribed to the polar effect due to the electronic influence of the electronegative bromine atom in the α-substituent.

In the case of AF agents exhibiting a low rate constant of fragmentation (e.g. β-pinene), it may be necessary to favor this process by reacting them with monomers having a low rate of copolymerization (e.g. cinnamates, maleic anhydride, etc.). For example, β-pinene was successfully copolymerized with maleic anhydride. Indeed, the addition step on β-pinene is slow enough to favor the ring-opening versus propagation (Scheme 37).

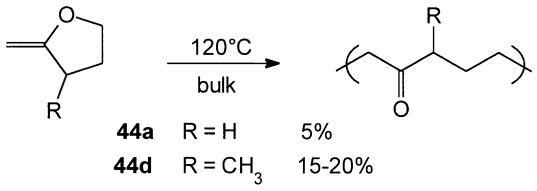
For compounds bearing unsaturation of lower reactivity, chain-transfer tendencies of the hydrogen atoms at the carbons next to the sulfur atom may be suspected to be important. To inhibit such side-reactions, it is generally recommended the use a sufficiently activated unsaturation, which can generate quickly a radical intermediate, avoiding large extent of allylic attack. However, Rizzardo et al. [33,52] reported recently the successful AF homopolymerization of inactivated allylic compounds **41i–m**. These latter AF monomers were shown to polymerize without degradative chain-transfer (through S_H2 of allylic hydrogen). This side-reaction may be inhibited when a fast fragmentation process rearranges the reactive carbon-centered adduct radicals into the softer sulfur-centered radical species. The latter are known to add selectively to unsaturations without allylic hydrogen abstraction. However, these AF monomers exhibit limited abilities to copolymerize with common vinylic monomers. To fulfill such a requirement, especially when a functional group has to be incorporated in the backbone of a vinylic polymer, the AF agent has to be reactive enough versus macroradicals, though incorporation through 1,2-addition polymerization must be avoided. The adduct radical formed through addition on the AF agent has to fragment readily to afford either an isomer radical (for polymerization) or two entities, a radical and a non-radical one (for chain transfer). The combination of a reactive unsaturation, protected



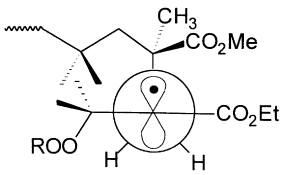
Scheme 38. AF homopolymerization of monomers **41g** and **51b**.

from copolymerization by steric hindrance, and a reactive fragmentable group in a given position on the same compound facilitates AF reaction. In the case of the homopolymerization of AF monomer in solution, the relative steric hindrance of the fragment attached at the α position may inhibit intermolecular propagation and facilitate fragmentation. The replacement of the methyl substituent at the α position of acrylic esters by an ethyl (or longer) moiety sterically disfavors propagation to a point where depolymerization competes effectively with propagation. The reactivities of α-substituted methyl acrylates toward PS· radicals decrease in the following order of the substituents Ph $\gg$ Me $>$ $PhCH_2$ $>$ H $\sim$ Et $\sim$ *n*-Pr $\sim$ *n*-Bu $>$ *i*-Bu $>$ *c*-Hex $>$ *i*-Pr $>$ *s*-Bu. The order can mostly be explained in terms of steric effect. Such a behavior is due to the fact that α-substituted acrylates exhibit a lower ceiling temperature T_c than usual acrylates. Reported T_c for MMA and 3-methylene-2-oxotetrahydropyrane are ca. 241°C and 154°C in bulk polymerization, respectively [103]. It is one of the reasons why most AF polymerizations are performed at high temperature ($T > 120$°C, in most cases) to approach or even exceed in some cases the ceiling temperature. The ceiling temperature also varies with dilution (Section 3.2). In the case of monomer **40**, once the initial adduct radical is formed, the intramolecular reaction occurs rapidly, with fragmentation of the ring and propagation through a new radical. While unfavorable in a thermodynamic sense, kinetic control overrides in the fragmentation of such monomers, and the new radical generated immediately propagates to form ring-opened structures in the polymer chain.

The presence of a substituent in α-position of the vinyl unsaturation of an AF monomer can also avoid crosslinking of the resulting polymers [92,184]. Indeed, this fragment is located on the double bond formed through fragmentation. The AF polymerization of **51b** and **41g** illustrates such a phenomenon, and can be conducted up to high conversion without gelation (Scheme 38). In this case, the methyl group is located on the double bond to afford a crotonate fragment and inhibits the formation of crosslinked



Scheme 39. Influence of allylic substituents in the AF homopolymerization of 2-methylenetetrahydrofuranyl derivatives **44**.



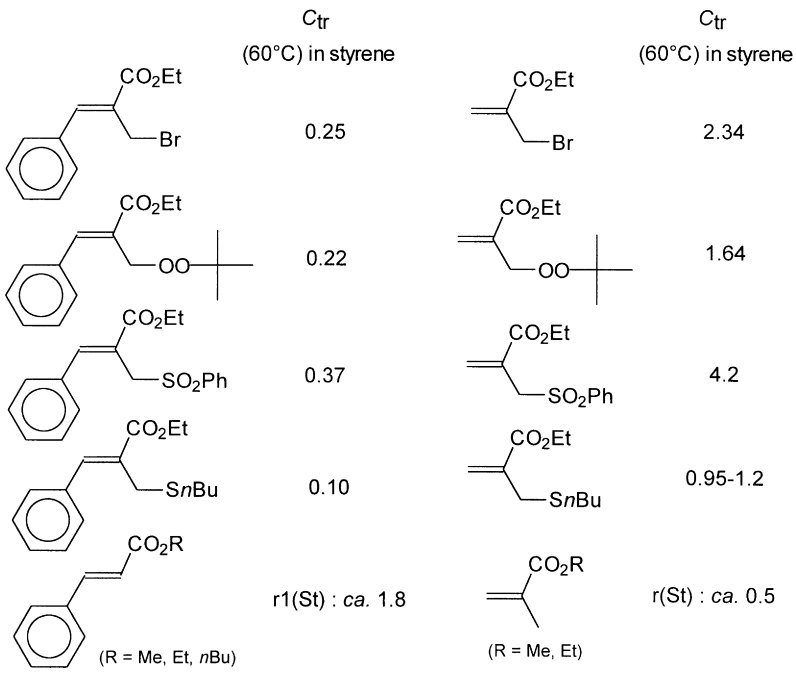
Scheme 40. Steric hindrance in the addition of PMMA radical on the unsaturation of a peroxydic-type AFCTA.

structures. It should, however, be noted that the reactivity of monomer **41g** bearing a methyl fragment in allylic position in copolymerization with MMA is also affected to some unnegligible extent.

Similarly, the AF homopolymerization of 2-methylenetetrahydrofuranyl derivatives **44** can be influenced by the presence of a methyl group in allylic position of the unsaturation. The addition of the primary radical resulting from β-scission on the unsaturation is favored, as compared to those of the tertiary adduct radical: the ratio k_{fr}/k_{21} is increased by a factor 3 or 4 in the polymerization of **44d**, compared to that of **44a** (Scheme 39).

It was also shown in the case of AF chain transfer that the reactivity of methacrylic-type AF reagents is very much influenced by α-substituents (fragment W-G-Z in Scheme 5 and Table 1) [12]. For example, substitution on the allylic position by peroxydic methacrylic-type AF chain transfer agents **5–7** decreases the rate of addition to the unsaturation to a large extent. The branching of the α-substituent on the other side of the peroxydic bond (fragment Z, Scheme 5, Table 1) does not severely influence the transfer properties. Such a phenomenon has been previously reported in copolymerization [185,186]. It has been illustrated in our laboratory by the comparison of steric hindrance between growing PS, PMMA and PBA radicals with the α-substituent on **5a–c**, in the addition step of the transfer reaction. The effect is particularly important in MMA in which peroxyketals **5a–c** exhibit chain transfer constants ten-folds lower (C_{tr} = ca. 0.1) than peroxides **2** and **3** (C_{tr} = 0.8–1.1). The steric hindrance between the methyl fragment of the growing PMMA radical and the fragment W-G-Z (Scheme 5, Table 1) on allylic peroxyketals was invoked to slow down the addition step of the transfer reaction [187,188] (Scheme 40). It can be noted that the decrease of the chain transfer properties is less marked in the case of **6a**, which may be explained by the favorable electron-withdrawing effect of the α-methoxy fragment on the electron-density of the unsaturation. Steric effect in the addition step was also less important in BA polymerization (no substitution in α) which can account for the satisfactory chain transfer constants obtained in the latter case.

2.2.1.2. Substitution on vinylic β-carbon It is well known that 1,2-disubstituted alkenes bearing a substituent at the point of attack (e.g. crotonate, cinnamate, stilbene, 1,2-dichloroethylene) are relatively reluctant to homopolymerize, although they do copolymerize readily. In the case of radical additions to such unsaturated compounds, a large steric effect arises. For example, the effects of disubstitution can be illustrated by the comparison between the addition of PS· radicals onto acrylic acid CH_2=$CHCO_2H$ and onto crotonic acid MeCH=$CHCO_2H$. The latter is 12 times more reactive with the former monomer. Similarly, the addition of a primary alkyl radical to methyl crotonate (i.e. methyl 2-butenoate) is very much slower (by a factor estimated to be ca. 100 at 60°C) than to methyl acrylate. We have shown recently that the reactivity of 2-(substituted)cinnamates [11], activated towards radical addition by two activating groups on the double bond and containing a homolytic leaving group in allylic position, was rather fair in styrene polymerization and was found to be inactive in MMA polymerization (Scheme 41).



Scheme 41. Comparison of the chain transfer activity of cinnamate-type and methacrylic-type addition–fragmentation agents.

However, the results obtained are in rather good agreement with the reciprocal of the reactivity ratios of the corresponding cinnamate monomers when copolymerized with St (Scheme 41), in agreement with the expected additional steric hindrance of leaving fragments.

2.2.1.3. Substitution on dienic carbons In the search for new AF agents capable of furnishing polymerizable macromonomers, we have examined the reactivity of various 5-substituted-1,3-pentadiene derivatives, i.e. 5-bromo-1,3-pentadienyl compounds **32a–d** and **36a**, 5-*tertio*-butylthio-1,3-pentadienyl-type derivatives **32a–d** and **36b**, and 5-*tertio*-alkylperoxy-1,3-pentadienes **9a–e**, bearing various substituents Y and/or Y′, in the free radical polymerizations of MMA and of styrene (Scheme 5, Table 5).

Many synergetic factors (i.e. resonance, polar and steric effects) have to be considered to quantify the addition efficiency on dienic AF chain transfer agents in radical polymerization. The importance of these factors depends on both the affinity of the propagating radicals towards the conjugated double bonds and the stabilization of the intermediate radical adduct, according to the nature of the substituents on the unsaturation, i.e. fragments Y, Y′ and CH_2-G-Z (Scheme 5). The substitution pattern (i.e. the presence of hydrogen atom, methyl or methoxycarbonyl groups as Y and/or Y′ groups) in the reactivity of **9**, **32** and **33** in the radical polymerization of MMA and St is a means to control: (1) the steric hindrance upon addition of the macroradical to the terminal methylene fragment of the CTA, (2) the increase of the electron density of the dienic unsaturation, (3) the stabilization of the intermediate allyl radical and its reactivity toward fragmentation, (4) the extent of the addition of the intermediate adduct radical to another monomer. The re-initiation step (i.e. by Br, S*t*Bu or O*t*Bu radicals) is not influenced by the substitution pattern on the corresponding AF transfer agents.

The two main criteria in the assessment of these transfer agents were the chain transfer efficiency in

Table 5
Comparison of the chain transfer constants (C_{tr}) and retardation[a] (R_p/R_{p0}) for $CH_2 = C(Y)CH = C(Y')–CH_2$-G-Z at 60°C in the radical polymerization of MMA and St[b]

AFCTA	Y	Y′	G-Z	C_{tr} (MMA)	C_{tr} (St)	Ref.
32a	H	H	Br	4.0 (0.44)	3.6 (0.82)	[34]
9a[c]	H	H	$OOCMe_2Ph$	3.2 (0.62)	1.0 (0.87)	[18]
33a	H	H	StBu	2.4 (0.29)	0.4 (0.63)	[35]
32b	Me	H	Br	8.3 (0.23)	4.3 (0.72)	[35]
9c[c]	Me	H	OOtBu	4.6 (0.22)	1.4 (0.89)	[19]
33b	Me	H	StBu	1.8 (0.17)	0.6 (0.74)	[35]
32c	H	Me	Br	8.8 (0.47)	4.9 (0.50)	[35]
33c	H	Me	StBu	4.5 (0.38)	1.1 (0.74)	[35]
32d	Me	Me	Br	6.1 (0.18)	2.1 (0.50)	[35]
9d[c]	Me	Me	OOtBu	3.2 (0.41)	0.6 (0.71)	[19]
33d	Me	Me	StBu	2.6 (0.33)	0.5 (0.74)	[35]
36a[c]	Me	CO_2Me	Br	7.4 (0.12)	8.1 (0.60)	[34]
9e[c]	Me	CO_2Me	$OOCMe_2Ph$	8.0 (0.10)	7.7 (0.40)	[19]
36b[d]	Me	CO_2Me	StBu	0.3 (0.10)	1.5 (0.10)	[29]
10	$CH_3(CH=CH)_2CH(OMe)OOCMe_2Ph$			0.1 (0.90)	0.14 (0.90)	[19]

[a] The ratio R_p/R_{p0} is given between parenthesis, and determined from the rate of polymerization with and without added AFCTA (the highest concentration of AFCTA used in polymerization is 10^{-1} mol l^{-1}).
[b] Polymerization conditions: 60°C, conversion $<$ 5%, [AIBN] $= 3 \times 10^{-3}$ mol l^{-1}.
[c] [AFCTA]maximum $= 10^{-2}$ mol l^{-1}.
[d] [AIBN]/[M] $= 10^{-3}$, [AFCTA]/[M] maximum $= 5 \times 10^{-3}$.

MMA and St polymerization, determined through the Mayo equation [189], and the extent of retardation effect. The latter has been estimated from the decrease of the conversion or from the ratio of the polymerization rates in the presence (R_p) and in the absence (R_{p0}) of dienic transfer agent. It has also been established that, in some cases, the copolymerization of the intermediate adduct radical competes with the fragmentation process [35]. Thus, the bromo derivatives **32a–d** and 5-cumylperoxy-1,3-pentadiene **9a** were shown to fragment readily without copolymerization. They afford either diene end-capped (**32**, **33**) or vinyloxirane end-capped (**9**) macromonomers by the AF process.

These groups were shown to be quantitatively introduced at the ω-end of the polymer by both elemental and spectroscopic analysis [19,34,35]. Chain length controlled PMMA prepared in the presence of **32a–d** exhibited a number of bromo atoms per chain close to unity, indicating the absence of copolymerization (Table 6). However, thioderivatives **33a–d** exhibit various degrees of copolymerization depending of the substitution pattern on dienic carbons (Table 6). Polymerizations of MMA conducted in the presence of **33a** and **33b** were shown to incorporate ca. 1.4 and 1.7 fragments, respectively, through 1,2-addition without fragmentation, and one fragment at the end of the chain in each case (functionality close to one). **33c** and **33d** copolymerize slightly when added to the bulk polymerization of MMA at 60°C or 80°C [35]. Such a behavior should be correlated with the presence of a methyl group on C^4.

Irrespective of the monomer used, the presence of **9**, **32** or **33** caused substantial retardation in the polymerization rate, which was compared to the retardation observed in classical copolymerization reactions. Indeed, such a retardation partly arises from the decrease of the rate of polymerization due to the addition step on the CTA, and not on the presence of degradative chain

Table 6
Influence of the substitution on dienic carbons on the degree of copolymerization and the functionality of **32** and **33** [35], used as AFCTA in the bulk polymerization of MMA at 60°C[a]

AFCTA	DP_n	C_{tr}	Number of Br or S per chain[b]	Average functionality[c]
32a	116	4.0	1.4	1.3
32b	115	8.3	1.4	1.1
32c	78	8.8	1.5	0.9
32d	165	6.1	1.7	0.8
> **33a**	330	2.4	2.4	0.9
33b	194	1.8	2.7	1.3
33c	77	4.5	1.5	1.5
33d	134	2.6	1.4	1.5

[a] Polymerization conditions: [AFCTA]/[MMA] = 2.8×10^{-3}; [AIBN]/[MMA] = 3.2×10^{-4}.
[b] Determined by elemental analysis.
[c] Determined by UV absorption of diene fragment, by comparison with blank PMMA, in solution in 2,2,2-trifluoroethane.

transfer. This phenomenon was illustrated by the comparison of the reactivity of **32** and **33** with that of *trans*-1,3-pentadiene, when copolymerized with MMA [35]. The extent of retardation (i.e. R_p/R_{p0}) is reported in Table 5, for [AFCTA]maxi = 0.1 mol l^{-1}. It has to be noted, however, that such a behavior does not affect the functionality (Table 6) and the utility of the resultant polymers as macromonomers [34,35].

In the case of the polymerization of St at 60°C in the presence of **32a–d**, the chain transfer constants appear slightly higher for **32b,c** versus the values obtained for **32a** (Table 5). This difference results from the sterically hindered 1,2-addition of the PS macroradical on **32b,c**, due to the presence of methyl substituents (Y or Y′). In the case of **32d**, the chain transfer constant is similar to that obtained in the presence of **32a**, which could be due to an inhibition of steric and electronic effects in the addition step.

With regard to the polymerization of MMA at 60°C in the presence of **9a–d**, **32a–d** and **33a–d**, the variation of C_{tr} is of the same order as that obtained in St (Table 5). The slightly electrophilic PMMA macroradical adds quickly on the electron-rich pentadienic unsaturation (i.e. particularly when substituted by inductive electron-donating methyl groups). The influence of the steric factor seems more important with the polymerization in the presence of **32b** (or **33b**) than **32c** (or **33c**, respectively). Such a phenomenon is also observed with peroxydic dienic chain transfer agents **9a–c**, but to a lower extent (Table 5).

The similarity observed upon comparing the chain transfer constant of PMMA radical on **33a** (C_{tr} = ca. 2.4) with the reciprocal of the copolymerization parameters of MMA (M_1, $1/r_1 = 2.3$ at 60°C) [181,190] with 1,3-pentadiene (M_2) seems to be fortuitous. Indeed, **33a** was shown to copolymerize and these two values cannot be compared directly. However, the higher C_{tr} of PMMA radical on **32a** (ca. 4.0) may be explained by the electron-withdrawing effect of the bromine atom which polarizes the dienic unsaturation and stabilizes the intermediary adduct radical. A similar difference of transfer properties was also observed in the polymerization of MMA in the presence of **21a** and **21b** (C_{tr} = 2.93 and 0.80, respectively) [27,32].

Introduction of methyl groups on the diene fragment results in a slight increase of the HOMO and the LUMO energies of the unsaturation by inductive electron-donating effect, which could explain the modification of the reactivity for **32b–d** and **33b–d** in comparison with their unsubstituted parents

32a and **33a**, in both MMA and St polymerization (Table 5). The highest value (ca. 8.8) obtained for the polymerization of MMA in the presence of **32c** (compared to **32b**, $C_{tr} = 8.3$ only) can be explained by a low difference of electron density of the unsaturation, and through the higher steric hindrance in the addition step of PMMA radicals on **32b** than on **32c**. The reactivity of **32d** in MMA (C_{tr} = ca. 6.1) seems to be controlled rather by the steric effect (of the methyl fragment on Y) than by the favorable polar factor resulting from the electron-donating inductive effect of two methyl fragment.

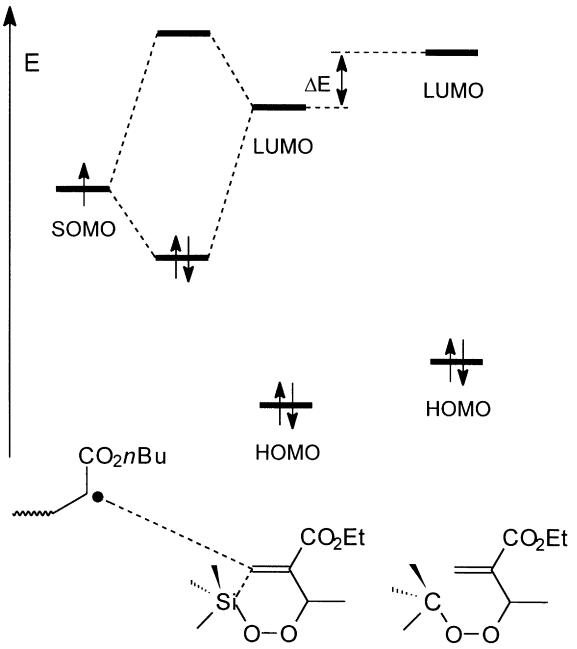
Relative C_{tr} obtained for **9a–d** and **33a–d** are in agreement with those of **32a–d**, with the exception of **33b** (C_{tr} = ca. 1.8) which is a bit lower than expected. Similarly, the results obtained with **9e** and **36a,b** in both MMA and St are rather difficult to comment and to compare with others. Transfer properties on **36b** are particularly surprising. Further kinetic investigations on the reactivity of these dienic compounds are under study in our laboratory.

The lower chain transfer activity of 6-cumylperoxy-6-methoxy-2,4-hexadiene **10** in St and MMA (ca. 0.14 and 0.09, respectively) [19], compared to those of 5-cumylperoxy-1,3-pentadiene **9a** (ca. 1.0 and 3.2, respectively) [18] is a further example of the effect of substituent on the carbon supporting the radical attack. The more important effect observed in MMA is explained by the higher steric hindrance between the PMMA · radical (α-methyl fragment) and the β-methyl substituent on the dienic peroxyketal, which slows the addition step of the transfer reaction.

2.2.1.4. Chain length dependence Moad et al. [191] have invoked a chain length dependence for C_{tr} when oligomers (particularly for very short chain lengths) add on AFCTA. For example, the marked difference in the reactivity of the primary propagating radical of styrene (i.e. $CH_3CH(Ph)\cdot$) and the propagating PS · macroradical of high molar-mass has been shown to arise from a difference of the absolute rate constants of the addition. Indeed, the propagation rate constants in the first few steps in polymerization are greater than $k_{p(overall)}$. In this case, the addition of the primary propagating radicals to the monomer is faster than that of the polymer radicals, with degrees of polymerization more than four. It can be expected that the addition rate of polymer radicals to the common monomers decreases as the chain length increases, in the early stage of propagation. In this case, chain transfer efficiency have to be determined on long-chain polymer radical (concentration of AF transfer agent and initiator being low enough to inhibit formation of small oligomers).

2.2.2. Complexation effect

In styrene polymerization, C_{tr} on peroxysilanes **7** and peroxyketals **5** (ca. 0.9) are in the same range as that of peroxide **2** (ca. 1.6), which may imply a slight influence of the steric effect on the addition of polystyryl radicals. It can also be noted that these chain transfer constants are close to 1.0, which involves an accurate control of the molar masses of polymers in batch polymerizations to high conversions [192]. In MMA, the chain transfer constant of peroxysilanes **7** (ca. 0.15) appeared also similar to those of the peroxyketals **5** (ca. 0.1). Taking into account that the transfer constant on peroxide **2** (non-substituted in allylic position) was ca. 0.63, these results can be explained by a greater steric hindrance between the growing PMMA · radicals and the bulkier α-substituent on allylic peroxysilanes and peroxyketals (Section 2.2.1.1). However, the steric effects are not the only factors which have to be invoked in poly(BA) regulation to explain the C_{tr} observed in the cases of peroxyketal **5a** (ca. 0.63) and peroxysilane **7a** (ca. 2.03). We have proposed the hypothesis that the anomalous increase of the chain transfer properties in the case of the peroxysilane versus **5a** could be due to an electronic interaction of



Scheme 42. Hypothesis of d–π bonding in radical addition to peroxysilane **7a**.

the d-orbitals of the silicon atom on the unsaturation. The occurrence of a d–π bonding may be invoked when the conformation of the molecule can favor the d-orbital interaction, to accept charge density from a π-system. Such an electronic effect would modify sufficiently the electron density of the double bond and would favor, therefore, the addition step of the poly(acrylyl) radicals (which are amphiphilic macroradicals) (Scheme 42).

3. Reaction conditions for efficient addition–fragmentation processes

One of the well-known principles in chemistry is Hammond's Postulate [120], which can be stated by the following abstract: "The transition states of exothermic reaction are generally reactant-like, whilst those of endothermic reaction steps are generally product-like". In the evolution of the intermediate adduct radicals in AF processes, two competitive reactions are possible: fragmentation or propagation. The transition state for an exothermic fragmentation step being located "early" in the process, the molecular structure of the intermediate species is close to the reactants, both in geometry and energy. Conversely, for an endothermic addition reaction, the transition state occurs later on the reaction coordinate, with a structure close to the products.

The close dependence of the outcome of the radical reactions on reaction conditions (i.e. temperature, dilution and nature of solvent, etc.) has been investigated both in organic and polymer chemistry [31,193]. The fragmentation process (i.e. unimolecular isomerization) competes with propagation, and the proportion of rearranged fragments in the polymer chain depends upon reaction conditions

Scheme 43. Equilibrium between propagation and depropagation, and subsequent fragmentation process.

for systems involving incomplete rearrangement. Unimolecular processes are generally favored by higher reaction temperatures and by the use of low monomer concentrations. In this case, the temperature and the dilution dependence of the AF reaction are expected to be different from that of propagation in copolymerization. These effects are discussed later and illustrated with examples. The application of this property is well-documented in the literature. These examples support the generality of the rule and confirm its utility in obtaining polymers with reduced concentrations of pendent non-fragmented moieties. Nonetheless, it only works well for reagents for which high tendency towards AF was already established at lower temperatures. In the case of AF monomers, examples of high molar-mass AF polymers with total absence of cyclic pendent units in a wide range of reaction conditions are rare [2].

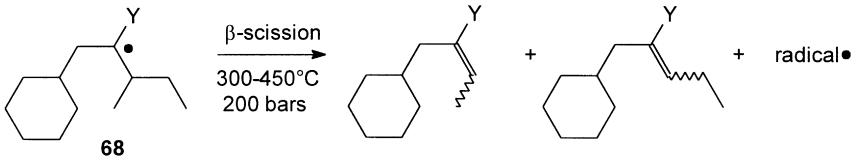
3.1. Effect of temperature

3.1.1. General aspects

Two types of fragmentation following the addition step have to be distinguished. The fragmentation of the adduct radical can either occur through depropagation, i.e. the reverse process of propagation, or through fragmentation of another weak bond of the molecule, different from the newly formed one (Scheme 43). Both of these are influenced by reaction conditions.

An increase of the temperature generally favors the reactivity of radical addition towards unsaturation (exothermic process), but disfavors the specificity (i.e. the reactivity–selectivity principle applies) [194]. An increase of the temperature also favors fragmentation entropically. It has been argued that, the enthalpy term being temperature independent (in the free-energy expression for the fragmentation process), the entropy term has a temperature factor (the entropy change being disfavored for ring-opening and favored for the intermolecular addition) and increasing temperature disfavors the latter more than fragmentation; that is, fragmentation is favored by default.

The ceiling temperature depends on dilution (Section 3.2). In the case of bulk polymerization of usual vinylic monomers, depropagation can be neglected at a temperature below 150°C. We have seen in



Y		
C_6H_5	5.3%	0.7%
p-$MeOC_6H_5$	6.65%	0.75%
p-ClC_6H_5	8.15%	0.85%
CO_2Me	13.9%	0.8%

Scheme 44. Yields (determined by capillary gas chromatography) of olefins obtained through intramolecular homolytic fragmentation of radicals **68**.

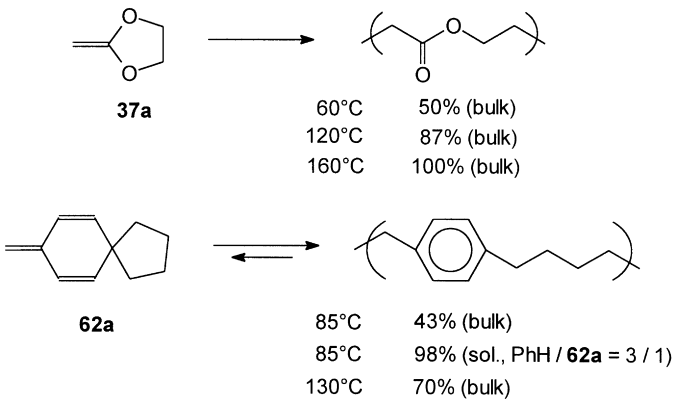
Section 2.1.1 that homopolymerization of AF reagents (i.e. transfer agents and monomers) bearing bulky groups in α-position was controlled through the depropagation of non-fragmented macroradicals, as a means to inhibit the incorporation of pendant fragment in the polymer.

For example, a very high temperature is generally required to get an effective β carbon–carbon bond fragmentation of a carbon-centered radical. Klenke et al. [195] have reported that the fragmentation of the carbon–carbon linkage in radical **68** may be achieved with low yields under extremely drastic reaction conditions (Scheme 44).

In the homopolymerization of methyl 2-phenoxymethyl propenoate [196,197], and of methyl 2-chloromethylpropenoate [198,199], fragmentation and propagation reactions occur simultaneously. The β-scission of the carbon-centered radical has to be carried out at relatively high temperatures in solution (>100°C). Fragmentation (i.e. a unimolecular reaction) and propagation (i.e. a bimolecular reaction) are influenced to various extents by an increase in temperature. The activation energy (E_a) and the pre-exponential factor (A) of methyl 2-phenoxymethylpropenoate and of methyl 2-chloromethylpropenoate for fragmentation and propagation were determined as follows: $E_{afr} - E_{ap} = 41.4$ and 34.0 kJ mol^{-1} and $A_{fr}/A_p = 5.5 \times 10^4$ and 2.0×10^4 mol l^{-1}, respectively [196,198].

Similarly, AF reactions reported by Watanabe et al. [200] and Yamada et al. [201] on dimers of α-methylstyrene and of MMA, respectively, were considerably accelerated at temperatures higher than 100°C and 140°C, in agreement with the higher activation energy of the fragmentation. The influence of the reaction temperature is illustrated in Scheme 45 by the modification of the extent of fragmentation in the bulk polymerization of compounds **37a** [37] and **62a** [134].

On the contrary, the exclusive AF polymerization of 2-phenyl-4-methylene-1,3-dioxolane **45c** to form poly(2-oxopropane) was performed by using photoinitiation at temperatures lower than 30°C. Indeed, under such conditions, the adduct radical on **45c** is not activated enough to undergo fast propagation and it rearranges to the more stable benzyl radical without further elimination reaction [63]. Comparatively, when **45c** is polymerized at 120°C in bulk, percentage yields of ring-opening structure and benzaldehyde elimination were 73% and 36%, respectively [38,65]. Under the same conditions (120°C), the AF polymerization of 2,2-diphenyl-4-methylene-1,3-dioxolane **45b** afforded the same polymer (i.e. poly(2-oxopropane)) in 100% yield [158], whereas the proportion of ring-opened fragments was only



Scheme 45. Influence of the temperature in the AFP of **37a** and **62a**.

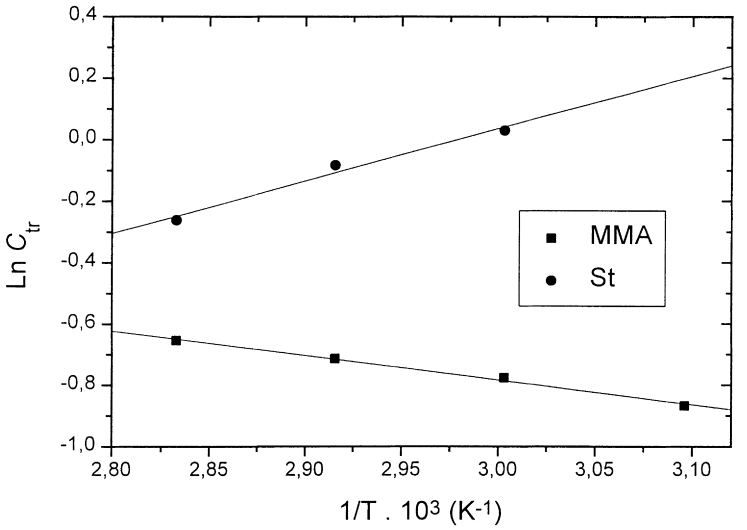


Fig. 1. Chain transfer constant neperien logarithm of PMMA and PS macroradicals on **6a** as a function of the reciprocal reaction temperature. The line is a least-square fit to the data represented by the filled circles.

18% at 60°C [158,202]. In these two latter cases, the stability of the system gained by the quantitative formation of benzophenone favors the elimination process through β_3-scission mentioned in Scheme 6.

Another consideration should not be overlooked whilst relative reactivity data are being discussed [203]. When the rates compared are rather similar, a closer approach may reveal that the observed differences are dominated by entropy effects, rather than by enthalpy effects. Thus, an inversion in reactivity orders can be observed when the temperature is variable. The temperature at which the two reactions have identical rates is called the "isoselective temperature". For example, we have examined the temperature dependence of relative reactivity of 3-cumylperoxy-3-methoxy-2-phenyl-1-propene **6a** towards PS· and PMMA· macroradicals [15]. The temperature dependence is such that the order of reactivity of these two radicals is expected to be reversed for temperatures below 30°C (Fig. 1). Similarly, peroxyketals **5a** and **5b** behave nearly as "azeotropic" transfer agents for styrene at 60°C (0.91 and 0.97, respectively) [12,13].

3.1.2. Thermolysis of addition–fragmentation agent—co-initiation effect

While we were pursuing the synthesis of new AF agents for generating new functionalized polymers, we decided to study the behavior of peroxyketal **5a** versus a large range of temperatures, in order to determine the thermodynamic parameters of the process [13]. It revealed a very low thermal degradation of peroxyketal **5a**, which occurred as a minor side-reaction during the polymerization [204]. This means that the polymerization has to be considered as being initiated by two initiators. The dependency of $(R_p/R_{p0})^2$ versus [CTA]/[MMA] is reported in Fig. 2 at temperatures varying from 60°C to 80°C.

Less than 1–2% of peroxyketal **5a** were found to homolyze under the usual reaction conditions (bulk, 60°C, 1–3 h), but the effects on the kinetics of polymerization were important, in comparison with the concentrations used (Fig. 2). For temperatures lower than 70°C, a decrease of the ratio $(R_p/R_{p0})^2$ is observed whereas for temperatures $>$ 70°C, an increase in the polymerization rate is observed. Clearly, the peroxydic bond co-initiates the radical polymerization of the monomer; these findings were

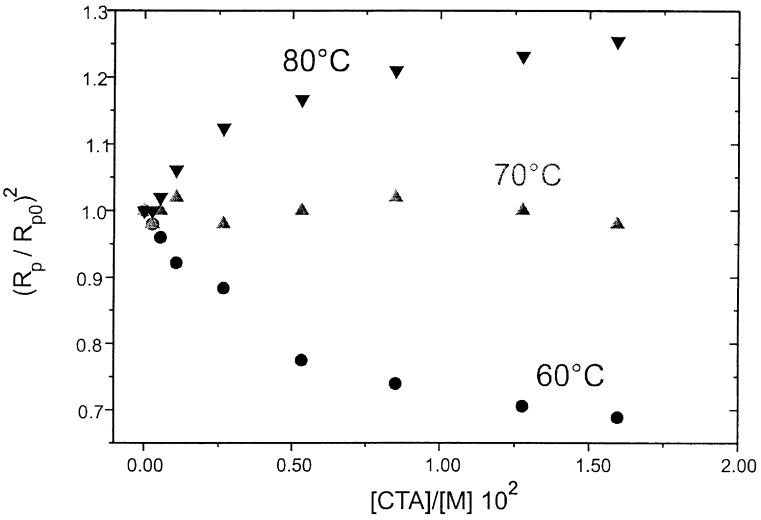
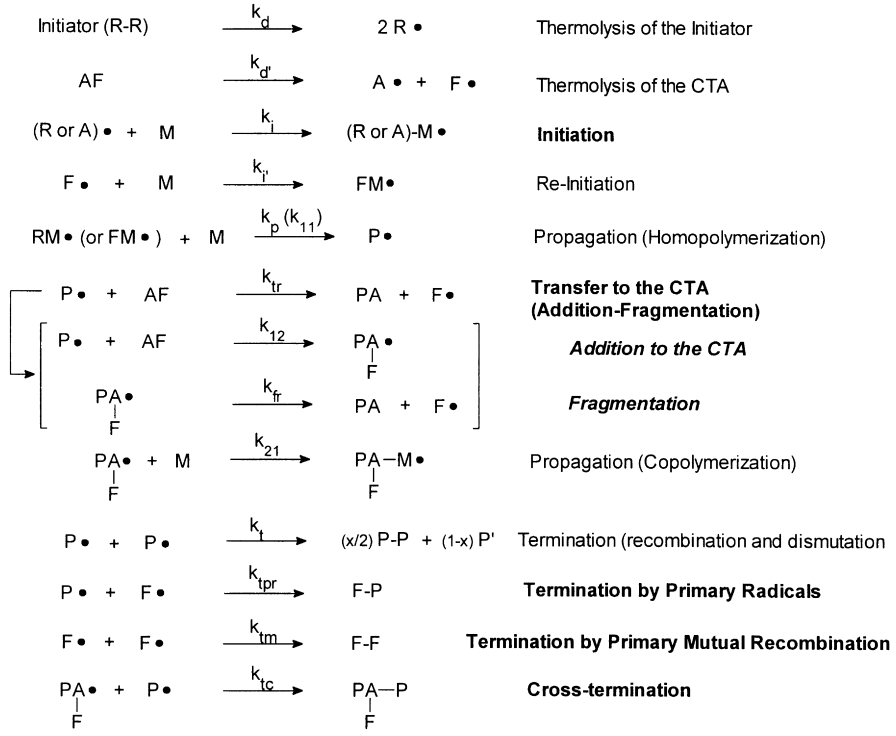
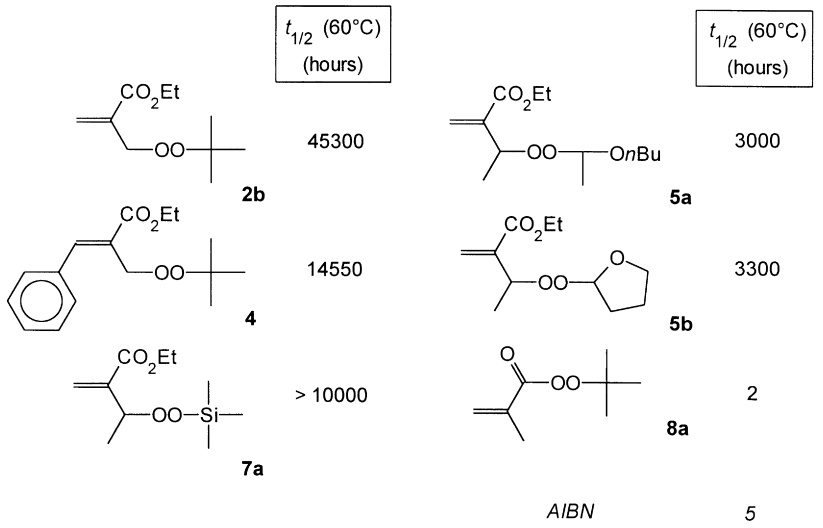


Fig. 2. Dependency of the square of the relative rates of polymerization $(R_p/R_{p0})^2$ of MMA versus the concentration of the addition–fragmentation agent **5a** at various temperature (●: 60°C, ▲: 70°C, ▼: 80°C).



Scheme 46. Elemental radical reactions involved in the polymerization of a monomer (M) in the presence of an AF chain transfer agent (noted “AF”).



Scheme 47. Half-life times ($t_{1/2}$) of peroxydic compounds, compared to AIBN.

confirmed by the use of higher concentrations of **5a** (up to 10^{-1} mol l^{-1}). All elemental reactions interfering in the system have to be considered to explain this unexpected behavior. The elemental reactions observed in most radical polymerizations involving AF transfer processes are reported in Scheme 46, in connection with those specifically observed in the presence of thermally unstable AF transfer agents. Half-life times of selected peroxycompounds versus temperature are reported in Scheme 47 as well [2].

An expression of the relative rate of polymerization was proposed for free radical polymerizations in the presence of an added initiator and **5a** which also act as an AF chain transfer agent (discussed later) [204]. Such a reaction may be considered as a special case where the AF agent also acts as an initiator with a thermolysis rate constant $k_{d'}$ (the efficiency factor of **5a** is noted f'). The kinetic model takes into account chain termination with a primary radical but excludes the mutual termination of primary radicals.

$$\left[\frac{R_p}{R_{p0}}\right]^2 = \frac{1 + A\dfrac{[CTA]}{[M]}}{1 + 2P\dfrac{[CTA]}{[M]}} \quad \text{where} \begin{cases} A = 2f' k_{d'} \dfrac{k_p^2}{k_t} \dfrac{[M]^3}{R_{p0}} \\ P = \dfrac{k_{tpr} k_{tr}}{k_t k_{i'}} \end{cases}$$

If we consider the concentrations of the added initiator and the monomer to be constant for all the experiments (low conversion), the values of R_{p0} and of the parameter A may be considered as constants as well (for a given temperature). Thus, this equation describes the variation of R_p as a function of the concentration of the AF agent. Chain length controlled polymerizations were performed at different temperatures to establish the validity of the equation [202]. The polymerization of MMA in the presence of **5a** exhibited retardation until 70°C, beyond which temperature the polymerization rate increased with increasing concentration of the AF agent (Fig. 2).

Table 7
Influence of dilution on the fragmentation efficiency of **33a**, used as AFCTA in the radical polymerization of MMA at 60°C[a,b]

Entry	Dilution (% toluene)	Reaction time (h)	Conversion (%)	DP_n	Number of S per chain[c]
1	0	1.3	1.5	85	/
2	30	2.2	1.5	65	3.5
3	57	16	14	97	3.0
4	79	41	20	90	1.3
5	90	163	22	104	1.2

[a] Reaction conditions: [**33a**]/[MMA] = 1.9×10^{-2}; [AIBN]/[MMA] = 3.2×10^{-4}.
[b] Polymers were isolated by preparative SEC.
[c] Determined by elemental analysis, by comparison with blank PMMA.

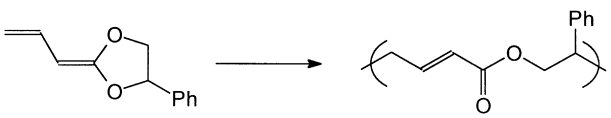
3.2. Dilution and solvent effect

The incorporation of a wide variety of functional groups into high molar-mass copolymers through AF processes can be provided by combinations of the previously reported effects. However, most of the time, it is not easy to maintain a good fragmentation efficiency when a monofunctional comonomer is present in the medium at high concentration. Indeed, the more monofunctional groups are present, the more likely intermolecular cross-propagation will occur rather than fragmentation. Such a phenomenon results in the formation of pendant cyclic functionalities that eventually perturb properties of the system. Of course, when the fragmentation efficiency is high enough, such a low concentration effect has little impact on the structure of well-defined ring-opened polymers, their yield being, however, lowered. For instance, the radical polymerization of **50e** carried out in the bulk or in solution (in benzene; concentration not specified), in the presence of AIBN as the initiator, afforded 91% and 94% of ring-opened units, respectively, in the polymer backbone, but the yields were only 37% and 13% accordingly, for the same reaction time (64 h). At higher temperature (120°C), gelation occurred.

We have shown recently that dilution may increase to a large extent the fragmentation efficiency of a dienic compound **33a**, used as AF transfer agent in the radical polymerization of MMA (Table 7). The number of sulfur atoms per chain, correlated to the presence of non-fragmented moieties in the PMMA backbone, decreases drastically with dilution. Such a behavior is in good agreement with expected results.

The nature of the solvent in radical processes can also show marked variation on the rates of propagation and the reactivity ratios in (co)polymerization (particularly when electron transfer is involved), according to the solvent employed [193]. Measurable solvent effects on vinylic monomers have been reported in the literature, but no systematic studies have been conducted in the case of AF agents.

An exclusive AF mechanism was also reported in the polymerization of an activated vinyl ketene



Scheme 48. AF polymerization of 4-phenyl-2-propenylene-1,3-dioxolane.

acetal, 4-phenyl-2-propenylene-1,3-dioxolane, carried out in very dilute solution to avoid crosslinking of the resulting polymer [205]. This diene acetal was thus constrained to polymerize through an AF process to afford *trans*-α β-unsaturated polyesters. Only 1,7-AFP was observed without any vinylic or dienic side-polymerization (Scheme 48) [206,207].

The ceiling temperature is also affected by dilution. Reported T_c values for MMA and 3-methylene-γ-valerolactone (i.e. 3-methylene-2-oxotetrahydropyran, non-fragmentable monomer considered as similar to AFM **41a**) are ca. 241°C and 154°C ([olefin] = 8.35 M), 218°C and 135°C ([olefin] = 5.0 M), and 160°C and 83°C ([olefin] = 1.0 M), respectively [103]. We have seen in Section 2.1.1 that such a factor could favor the occurrence of fragmentation processes when vinylic homopropagation is a competitive side-reaction of the AF process.

4. Concluding remarks

AF processes offer an effective method for the formation of telechelic polymers through AF chain transfer, and the preparation of linear or crosslinked backbone structures up to high molar masses through AF polymerization. This latter process makes available a novel approach to copolymers containing ring-opened structures that have potential use in applications as diverse as biomaterials, dental cement and contact lenses. To achieve efficiently such a process, residual pendent fragments bearing functionality have to be at least hardly restricted or even suppressed.

In the present work, we examined the additional reagents from an empirical and synthetic perspective, to extend the aforementioned findings. That is, rather than worrying too much about the theoretical or physical/chemical aspects of target agents for AF capability, it is often better to just make the materials and see how they behave. To fulfill such a requirement, we are trying to incorporate various fragmentable groups at the α methylene position of various AF agents.

The understanding of factors controlling AF efficiency have been presented in this review, and future research in this field would be significantly enhanced by taking into account the requirements given before. The extension and application of these results may have potential for developing new industrial products.

Incorporation of molecular structures bearing specific functions into vinylic-type addition polymers may lead to sufficient enhancement of chemical properties. For example, the degradability of macromolecular architecture through enzymatic or chemical ways is an important field of research of our laboratory. Biological applications, involving incorporation of hydrolytically divisible drug molecules into intrinsically bioactive polymers could also find general utility.

As is the case in most scientific fields, step by step advances have occurred in the AF techniques. First, a rapid expansion of knowledge gave rise, in a second step, to an application plateau (i.e. the utilization of the method to prepare macromonomers, to control the growth of chains, etc.). However, the interest can decrease quickly if new applications are not identified. A new advance is needed now. A better understanding of the molecular control may catalyze a resurgence of interest in this area and a corresponding expansion in commercial potential. Such a resurgence is needed now and can be attained by the use of simple rules and by the understanding of AF efficiency that have been elucidated in the present article. We have to decide now whether or not sufficient interest in new materials still exists in the chemical industry, given the severe financial constraints that predominate (in most research and

developments departments) for managing companies, to allow research and application of new AF agents and their corresponding materials.

Acknowledgements

The author is grateful to Prof. P. Rempp for his help in reviewing this manuscript.

References

[1] Moad G, Solomon DH. The chemistry of free radical polymerization. London: Pergamon, 1995.
[2] Colombani D, Chaumont P. Progr Polym Sci 1996;21:439.
[3] Colombani D, Chaumont P. Acta Polymerica 1998;49:225.
[4] Butler GB. Cyclopolymerization and cyclocopolymerization. New York: Marcel Dekker, 1992.
[5] Nair CPR, Richou MC, Chaumont P, Clouet G. Eur Polym J 1990;26:811.
[6] Russell GA. In: Kochi JK, editor. Free radicals, 1. New York: Wiley, 1973. pp. 275.
[7] Berti C, Grierson L, Grimes JAM, Perkins MJ, Terem B. Angew Chem Int Ed Engl 1990;29:653.
[8] Brandrup J, Immergut EH, editors. Polymer handbook. 3. New York: Wiley Interscience, 1989 p. II-90-93.
[9] Vertommen LLT, Meijer J. PCT Int. Appl. WO 9107,440 (1991), Chem Abstr 115 (1991) 160038q.
[10] Meijs GF, Rizzardo E, Thang SH. Polym Prepr (Am Chem Soc Div Polym Chem) 1992;33(1):893.
[11] Colombani D, Chaumont P. Macromol Chem Phys 1995;196:3643.
[12] Colombani D, Chaumont P. J Polym Sci Part A: Polym Chem 1994;32:2687.
[13] Colombani D, Chaumont P. Macromolecules 1994;27:5972.
[14] Colombani D, Chaumont P. Polymer 1995;36:129.
[15] Colombani D, Zink MO, Chaumont P. Macromolecules 1995;29:819.
[16] Colombani D, Beliard I, Chaumont P. J Polym Sci Part A: Polym Chem 1996;34:893.
[17] Colombani D, Chaumont P. Macromol Chem Phys 1995;196:947.
[18] Colombani D, Chaumont P. Designed Monomers and Polymers 1998;1:65–75.
[19] Colombani D, Boiteau L, Chaumont P, Charmot D. Submitted to Macromolecules.
[20] Colombani D, Lamps JP, Chaumont P. Macromol Chem Phys 1998;199:2517.
[21] Meijs GF, Rizzardo E. Makromol Chem Rapid Commun 1988;9:547.
[22] Meijs GF, Rizzardo E, Thang SH. Makromol Chem 1990;191:1545.
[23] Meijs GF, Rizzardo E, Le TPT. Polymer Int 1991;26:239.
[24] Meijs GF, Rizzardo E. Polym Bull (Berlin) 1991;26:291.
[25] Bailey WJ, Endo T, Gapud B, Lin Y-N, Ni Z, Pan C-Y, Shaffer SE, Wu S-R, Yamazaki N, Yonezawa K. J Macromol Sci Chem 1984;A21(8-9):979.
[26] Yamada B, Kobatake S, Otsu T. Polym J (Tokyo) 1992;24:281.
[27] Meijs GF, Rizzardo E. Polym Bull (Berlin) 1990;24:501.
[28] Meijs GF, Morton TC, Rizzardo E, Thang SH. Macromolecules 1991;24:3689.
[29] Jiang S, Viehe HG, Oger N, Charmot D. Macromol Chem Phys 1995;196:2349.
[30] Sato T, Seno M, Kobayashi M, Kohno T, Tanaka H. Eur Polym J 1995;31:29.
[31] Odian G. Principles of polymerization. 3. New York: Wiley, 1991.
[32] Meijs GF, Rizzardo E, Thang SH. Macromolecules 1988;21:3122.
[33] Rizzardo E, Chong YK, Evans RA, Moad G, Thang SH. Macromol Chem Macromol Symp 1996;111:1.
[34] Zink MO, Colombani D, Chaumont P. Eur Polym J 1997;33:1433.
[35] Zink MO, Colombani D, Chaumont P, Charmot D. Submitted to Macromolecules.
[36] Nair CPR, Chaumont P, Charmot D. J Polym Sci Part A: Polym Chem 1995;33:2773.
[37] Bailey WJ, Chen PY, Chen S-C, Chiao W-B, Endo T, Gapud B, Lin Y-N, Ni Z, Pan C-Y, Shaffer SE, Sidney L, Wu S-R, Yamamoto N, Yamazaki N, Yonezawa K. J Macromol Sci Chem 1984;A21(13-14):1611.

[38] Bailey WJ. In: Allen G, Bevington JC, editors. Comprehensive polymer science; chain polymerization, Part I, 3. 1988 p. 283, Chapter 22.
[39] Bailey WJ, Ni Z, Wu SR. J Polym Sci Polym Chem Ed 1982;20:2420.
[40] Yako N, Endo T. Polym Prepr Jpn 1985;34:154.
[41] Bailey WJ, Wu SR, Ni Z. Macromolecules 1982;15 :711.
[42] Endo T, Yako N, Azuma K, Nate K. Makromol Chem 1985;186:1543.
[43] Bailey JW, Chen PY, Chen S-C, Chiao W-B, Endo T, Gapud B, Kuruganti V, Lin Y-N, Ni Z, Pan C-Y, Shaffer SE, Sidney L, Wu S-R, Yamamoto N, Yamazaki N, Yonezawa K, Zhou L. Makromol Chem Macromol Symp 1986;6:81.
[44] Bailey WJ, Ni Z, Wu SR. J Polym Sci Polym Chem Ed 1982;20:2420.
[45] Yokozawa T, Hayashi R, Endo T. J Polym Sci Polym Chem Ed 1990;28:3739.
[46] Schulze T, Klemm E. Polym Bull (Berlin) 1993;31:409.
[47] Schulze T, Klemm E. Macromol Chem Phys 1995;196:567.
[48] Bailey WJ, Chou JL, Feng PZ, Issari B, Kuruganti U, Zhou L-L. J Macromol Sci Chem 1988;A25(5-7):781.
[49] Rizzardo E, Evans RA, Moad G, Thang SH. PCT Int. Appl WO 94/14792, 1994.
[50] Evans RA, Moad G, Rizzardo E, Thang SH. Macromolecules 1994;27:7935.
[51] Colombani D, Baudouin A, Asgarzadeh F, Chaumont P. Macromol Chem Phys 1998;199:2577.
[52] Evans RA, Rizzardo E. Macromolecules 1996;29:6983.
[53] Evans RA, Rizzardo E. PCT Int. Appl. AU95/00859, 1995.
[54] Endo T, Bailey WJ. J Polym Sci Polym Symp 1978;64:17.
[55] Endo T, Bailey WJ. J Polym Sci Polym Lett Ed 1975;13:193.
[56] Endo T, Suga K. J. Polym. Sci. Polym. Chem. Ed. 1989;27:1831.
[57] Sanda F, Takata T, Endo T. Polym Prep Jpn 1991;40:1776.
[58] Endo T, Okawara M, Yamazaki N, Bailey WJ. J Polym Sci Polym Chem Ed 1981;19:1283.
[59] Pan CY, Ru SX. Makromol Chem 1987;188:1651.
[60] Gong MS, Chang SI, Cho I. Makromol Chem Rapid Commun 1985;10:201.
[61] Bailey WJ. Polym J 1981;17:85.
[62] Salon MC, Gandini A, Gey C. Makromol Chem Rapid Commun 1988;9:539.
[63] Cho I, Kim BG, Park YC, Kim CB, Gong MS. Makromol Chem Rapid Commun 1991;12:141.
[64] Moraniu S, Buruiana EC, Simionescu BC. Polym Bull (Berlin) 1993;30:7.
[65] Pan CY, Wu Z, Bailey WJ. J Polym Sci Part C: Polym Lett 1987;25:243.
[66] Hiraguri Y, Sugizaki T, Endo T. Macromolecules 1990;23:1.
[67] Hiraguri Y, Endo T. J Polym Sci Part A: Polym Chem 1990;28:2881.
[68] Hiraguri Y, Endo T. J Polym Sci Part A: Polym Chem 1989;27:4403.
[69] Takahashi T, Yamashita I. J Polym Sci Part B 1965;3:251.
[70] Takahashi T. J Polym Sci Part A-1 1968;6:403.
[71] Takahashi T, Yamashita I. Bull Chem Soc Jpn 1964;37:131.
[72] Endo T, Suga K. J. Polym. Sci. Part A: Polym. Chem. 1989;27:1831.
[73] Endo T, Watanabe M, Suga K, Yokozawa T. Makromol Chem 1989;190:691.
[74] Cho I, Ahn KD. J. Polym. Sci. Polym. Lett. Ed. 1977;15:751.
[75] Cho I, Ahn KD. J. Polym. Sci. Polym. Lett. Ed. 1979;17:3169.
[76] Endo T, Watanabe M, Suga K, Yokozawa T. J Polym Sci Part A: Polym Chem 1989;27:1435.
[77] Sanda F, Takata T, Endo T. Macromolecules 1995;28:1346.
[78] Sugiyama J, Ohashi K, Ueda M. Macromolecules 1994;27:5543.
[79] Sugiyama J, Kayamori N, Shimada S. Macromolecules 1996;29:1943.
[80] Cho I, Lee JY. Makromol Chem Rapid Commun 1984;5:263.
[81] Sanda F, Takata T, Endo T. Macromolecules 1994;27:3986.
[82] Kennedy JP, Elliott JJ, Butler PE. J Macromol Sci Chem 1968;A2:1415.
[83] Zhulin VM, Gonkberg MG, Volchek AR, Nefedox OM, Shashkov AS. Vysokomol Soyed, Ser A 1971;13:2153.
[84] Endo T, Yokozawa T. In: Mijs WJ, editor. New methods for polymer synthesis, New York: Plenum Press, 1992.
[85] Sanda F, Takata T, Endo T. Macromolecules 1994;27:1099.
[86] Mizukami S, Kihara N, Endo T. J Am Chem Soc 1994;116:6453.
[87] Sanda F, Murata J, Endo T. Macromolecules 1997;30:160.

[88] Sanda F, Takata T, Endo T. Macromolecules 1994;27:1099.
[89] Hiraguri Y, Endo T. J Polym Sci Part C: Polym Lett 1989;27:333.
[90] Cho I, Kim JB. J Polym Sci Polym Chem Ed 1983;21:433.
[91] Endo T, Kanda N. J Polym Sci Polym Chem Ed 1985;23:1931.
[92] Koizumi T, Nojima Y, Endo T. J Polym Sci Part A: Polym Chem 1993;31:3489.
[93] Suga K, Endo T. Polym Prepr Jpn 1987;36:140.
[94] Cho I, Lee MH. J Polym Sci. Polym Lett Ed 1987;25:309.
[95] Cho I. Makromol Chem. Macromol Symp 1990;33:45.
[96] Lautenschlaeger F, Schnecko H. J Polym Sci Part A-1. 1970;8:2579.
[97] Suga K, Endo T. Polym Prepr Jpn 1988;37:348.
[98] Yamada B, Otsu T. Makromol Chem 1991;192:333.
[99] Hansch C, Leo AJ. Substituent constants for correlation analysis in chemistry and biology. New York: Wiley, 1979 p. 65.
[100] Charton M. J Am Chem Soc 1969;91:615.
[101] Yamada B, Kobatake S. Prog Polym Sci 1994;19:1089.
[102] Chikanishi K, Tsuruta T. Makromol Chem 1965;81:198.
[103] Penelle J, Padias AB, Hall HK, Tanaka H. Adv Polym Sci 1992;102:75.
[104] Sugiyama J-I, Yokozawa T, Endo T. J Polym Sci Part A: Polym Chem 1990;28:3529.
[105] Beckwith ALJ. Tetrahedron 1981;37:3073.
[106] Sanda F, Takata T, Endo T. J Polym Sci Part A: Polym Chem 1993;31:2659.
[107] Endo T, Bailey WJ. J Polym Sci Polym Lett Ed 1975;13:193.
[108] Sato T, Morita N, Tanaka H, Ota T. Makromol Chem 1990;191:2599.
[109] Fukuda H, Hirota M, Endo T, Okawara M, Bailey WJ. J Polym Sci Polym Chem Ed 1982;20:2935.
[110] Beckwith ALJ, Ingold KU. In: de Mayo P, editor. Rearragement in ground and excited states, 1. New York: Academic Press, 1980 p. 162.
[111] Beckwith ALJ. Chem Soc Rev 1993:143.
[112] Colombani D, Maillard B. Tetrahedron 1996;52:14855.
[113] Huang XL, Dannenberg JJ. J Org Chem 1991;56:5421.
[114] Houk KN, Tucker JA, Dorigo AE. Acc Chem Res 1990;23:107.
[115] Sadhir RK, Luck RM, editors. Expanding monomers: synthesis, characterization, and applications Boca Raton, FL: CRC Press, 1992.
[116] Newcomb M. Tetrahedron 1993;49:1151.
[117] Beckwith ALJ, Bowry VW. J Am Chem Soc 1994;116:2710.
[118] Martin-Esker AA, Johnson CC, Horner JH, Newcomb M. J Am Chem Soc 1994;116:9174.
[119] Perkins MJ. Radical chemistry. New York: Ellis Horwood, 1994.
[120] Hammond GS. J Am Chem Soc 1955;77:334.
[121] Sabatino EC, Gritter RJ. J Org Chem 1963;28:3437.
[122] Rawal VH, Newton RC, Krishnamurthy V. J Org Chem 1990;55:5181.
[123] Davies AG, Hawari JAA, Muggleton B, Tse MW. J Chem Soc Perkin Trans 2 1981:1132.
[124] Trost BM. Top Curr Chem 1986;133:3.
[125] Hill EA, Chen AT, Doughty A. J Am Chem Soc 1976;98:167.
[126] Hiraguri Y, Endo T. J Polym Sci Polym Lett Ed 1988;26:381.
[127] Beckwith ALJ, Moad G. J Chem Soc Perkin Trans 2 1980;2:1473.
[128] Masnovi J, Samsel EG, Bullock RM. J Chem Soc Chem Commun 1989:1044.
[129] Jung ME, Gervay J. J Am Chem Soc 1991;113:224.
[130] Beckwith ALJ, Moad G. J Chem Soc Perkin Trans 2 1980:1083.
[131] Pryor WA, editor. Free radicals in biology, I–V. New York: Academic Press, 1976–1982.
[132] Errede LA. J Polym Sci 1961;49:253.
[133] Cho I, Song KY. J Polym Sci Part A: Polym Chem 1994;32:1789.
[134] Bailey WJ, Amone MJ, Chou JL. Polym Prepr (Am Chem Soc Div Polym Chem) 1988;29(1):178.
[135] Issari B, Bailey WJ. Polym Prepr (Am Chem Soc Div Polym Chem) 1988;29(1):217.
[136] Bailey WJ, Chou JL. In: Seymour RB, Mark HF, editors. Applications of polymers, New York: Plenum Press, 1988 p. 79.
[137] Bailey WJ, Chou JL. Polym Mater Sci Eng 1987;55:30.

[138] Barclay LRC, Griller D, Ingold KU. J Am Chem Soc 1982;104:4399.
[139] Colombani D. Progr Polym Sci 1997;22:1649.
[140] Dais VA, Priddy DB, Bell B, Sikkema KD, Smith P. J Polym Sci Part A: Polym Chem 1993;31:901.
[141] Sanda F, Takata T, Endo T. Macromolecules 1992;25:6719.
[142] Sanda F, Takata T, Endo T. Macromolecules 1993;26:1818.
[143] Mizukami S, Kihara N, Endo T. J Am Chem Soc 1994;116:6453.
[144] Tsang R, Dickson Jr JK, Pak H, Walton R, Fraser-Reid B. J Am Chem Soc 1987;109:3484.
[145] Takahashi T, Yamashita I. J Polym Sci Part B. 1965;3:251.
[146] Cho I, Kim JB. J Polym Sci Polym Chem Ed 1983;21:433.
[147] Endo T, Kanda N. J Polym Sci Polym Chem Ed 1985;23:1931.
[148] Tanaka H. Trends Polym Sci 1993;1:361.
[149] Viehe HG, Merenyi R, Stella L, Janousek Z. Angew Chem Int Ed Engl 1979;18:917.
[150] Nair CPR, Chaumont P, Charmot D. J Polym Sci Polym Chem 1995;32:2773.
[151] March J. Advanced organic chemistry. London: Wiley Interscience, 1985 p. 23.
[152] Yokozawa T, Hayashi R, Endo T. J Polym Sci Polym Chem Ed 1990;28:3739.
[153] Cho I, Lee MH. J Polym Sci Polym Lett Ed 1987;25:309.
[154] Cho I. Makromol Chem Macromol Symp 1990;33:45.
[155] Cho I, Kim BG, Park YC, Kim CB, Gong MS. Makromol Chem Rapid Commun 1991;12:141.
[156] Pan CY, Wu Z, Bailey WJ. J Polym Sci Part C: Polym Lett 1987;25:243.
[157] Moraniu S, Buruiana EC, Simionescu BC. Polym Bull (Berlin) 1993;30:7.
[158] Hiraguri Y, Endo T. J Am Chem Soc 1987;109:3779.
[159] Hiraguri Y, Endo T. J Polym Sci Polym Chem Ed 1989;27:2135.
[160] Tedder JM, Walton JC. Tetrahedron 1980;36:701.
[161] Tedder JM. Angew Chem Int Ed Engl 1982;21:401.
[162] Curran DP. In: Trost B, Fleming I, editors. Comprehensive organic synthesis, IV. London: Pergamon Press, 1982. pp. 715 Chapter 4.
[163] Beckwith ALJ, Easton CJ, Serelis AK. J Chem Soc Chem Commun 1980:482.
[164] Giese B. Angew Chem Int Ed Engl 1983;22:753.
[165] Tedder JM. Tetrahedron 1982;38:313.
[166] Beckwith ALJ. Tetrahedron 1981;37:3073.
[167] Bailey WJ, Chou JL, Feng PZ, Issari B, Kuruganti U, Zhou L-L. J Macromol Sci-Chem 1988;A25(5-7):781.
[168] Giese B. Radicals in organic synthesis: formation of carbon–carbon bonds. London: Pergamon Press, 1988.
[169] Brandrup J, Immergut EH, editors. Polymer handbook 3. New York: Wiley Interscience, 1989. pp. 153 p. II.
[170] Lussi H. Makromol Chem 1967;103:68.
[171] Yamada B, Otsu T. Makromol Chem 1991;192:333.
[172] Ueda M, Koyama T, Mano M, Yazawa M. J Polym Sci Part A: Polym Chem 1989;27:751.
[173] Kress AO, Mathias LJ, Cei G. Macromolecules 1989;22:537.
[174] Chikanishi K, Tsuruta T. Makromol Chem 1965;81:211.
[175] Yamada B, Kobatake S, Aoki S. Macromol Chem Phys 1994;195:933.
[176] Yamada B, Satake M, Otsu T. Makromol Chem 1991;192:2713.
[177] Yamada B, Kobatake S, Aoki S. Polymer 1994;35:1245.
[178] Sato T, Kamiya I, Tanaka H, Ota T. Eur Polym J 1991;27:1097.
[179] Braun D, Czerwinski W, Disselhoff G, Tudos F, Kelen T, Turcsanyi B. Angew Makromol Chem 1984;125:161.
[180] Boudevska H, Todorova O. Makromol Chem 1985;186:1711.
[181] Petit A. Eur Polym J 1993;29:1419.
[182] Paxton TR. J Polym Sci B1 1963:73.
[183] Zubov VP, Valuev LI, Kabanov VA, Kargin VA. J Polym Sci A1 1971;9:833.
[184] Koizumi T, Hasegawa Y, Takata T, Endo T. J Polym Sci Part A: Polym Chem 1994;32:3193.
[185] Brand E, Stickler M, Meyerhoff G. Makromol Chem 1980;181:913.
[186] Otsu T, Yamada B, Fujita M, Okuo M. J Polym Sci Part A: Polym Chem 1991;29:837.
[187] Cheng JS, Yamada B, Otsu T. J Polym Sci Part A: Polym Chem 1991;29:1837.
[188] Penelle J, Collot J, Rufflard GJ. J Polym Sci Part A: Polym Chem 1993;31:2407.

[189] Mayo FR. J Am Chem Soc 1943;65:2324.
[190] Petit A, Neel J. J Polym Sci Polym Chem Ed 1986;24:883.
[191] Moad CL, Moad G, Rizzardo E, Thang SH. Macromolecules 1996;29:7717.
[192] Corner T. Adv Polym Sci 1984;62:95.
[193] Martin JC. In: Kochi JK, editor. Free radicals, 2. New York: Wiley, 1973 p. 493.
[194] Giese B, Meister J. Angew Chem Int Ed Engl 1977;16:178.
[195] Klenke K, Metzger JO, Lübben S. Angew Chem Int Ed Engl 1988;27:1168.
[196] Yamada B, Satake M, Otsu T. Polym J (Tokyo) 1992;24:563.
[197] Yamada B, Kobatake S, Satake M, Otsu T. J Polym Sci Part A: Polym Chem 1993;31:1551.
[198] Yamada B, Kabatake S, Aoki S. Macromolecules 1993;26:5099.
[199] Yamada B, Kabatake S, Aoki S. Macromol Chem Phys 1994;195:933.
[200] Watanabe Y, Ishigaki H, Okada H, Suyama S. Chem Lett 1993:1089.
[201] Yamada B, Tagashira S, Aoki S. J Polym Sci Part A: Polym Chem 1994;32:2745.
[202] Hiraguri Y, Endo T. J Polym Sci Part A: Polym Chem 1992;30:689.
[203] Giese B. Acc Chem Res 1984;17:138.
[204] Nair CPR, Colombani D, Chaumont P. Macromolecules 1995;28:3192.
[205] Acar MH, Nambu Y, Yamamoto K, Endo T. J Polym Sci Polym Chem Ed 1989;27:4441.
[206] Cho I, Kim SK. J Polym Sci Part C: Polym Lett 1990;28:417.
[207] Fukuda H, Oda M, Endo T. Macromolecules 1995;28:4319.